VOLUME 9 • NUMBER 4 • APRIL, 1938

METALS and ALLOYS

The Magazine of Metallurgical Engineering

PRODUCTION • FABRICATION • TREATMENT • APPLICATION

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Published Monthly by Reinhold Publishing Corporation, East Stroudsburg, Pa., U.S.A. Ralph Reinhold, President and Treasurer; H. Burton Lowe, Vice President and Secretary; Philip H. Hubbard, Vice President; Francis M. Turner, Vice President. Executive and Editorial Offices, 330 West 42nd Street, New York. Price 40 cents a copy. Annual Subscription: U. S., Possessions and Canada, $3.00. All Other Countries, $4.00. (Remit by New York Draft). Copyright, 1938, by Reinhold Publishing Corporation. All rights reserved. Entered as second class matter June 12, 1934, at the Post Office at East Stroudsburg, Pa., under the Act of March 3, 1879.

ARTICLES

A Slagging Test for Refractories 79
HOBART M. KRANER

Seventh Report on the Heterogeneity of Steel Ingots . . 85
FRED P. PETERS

Low Temperature Impact Properties of Some S.A.E. Steels 90
A. J. HERZIG AND R. M. PARKE

Beryllium-Aluminum Alloys for Aircraft Pistons 94
J. B. JOHNSON

Protecting Metal Surfaces with Modern Lacquers and Enamels 95
G. KLINKENSTEIN

Use of Electron Diffraction in Studying Corrosion—II . 100
I. R. LANDAU

Letters to the Editor 104

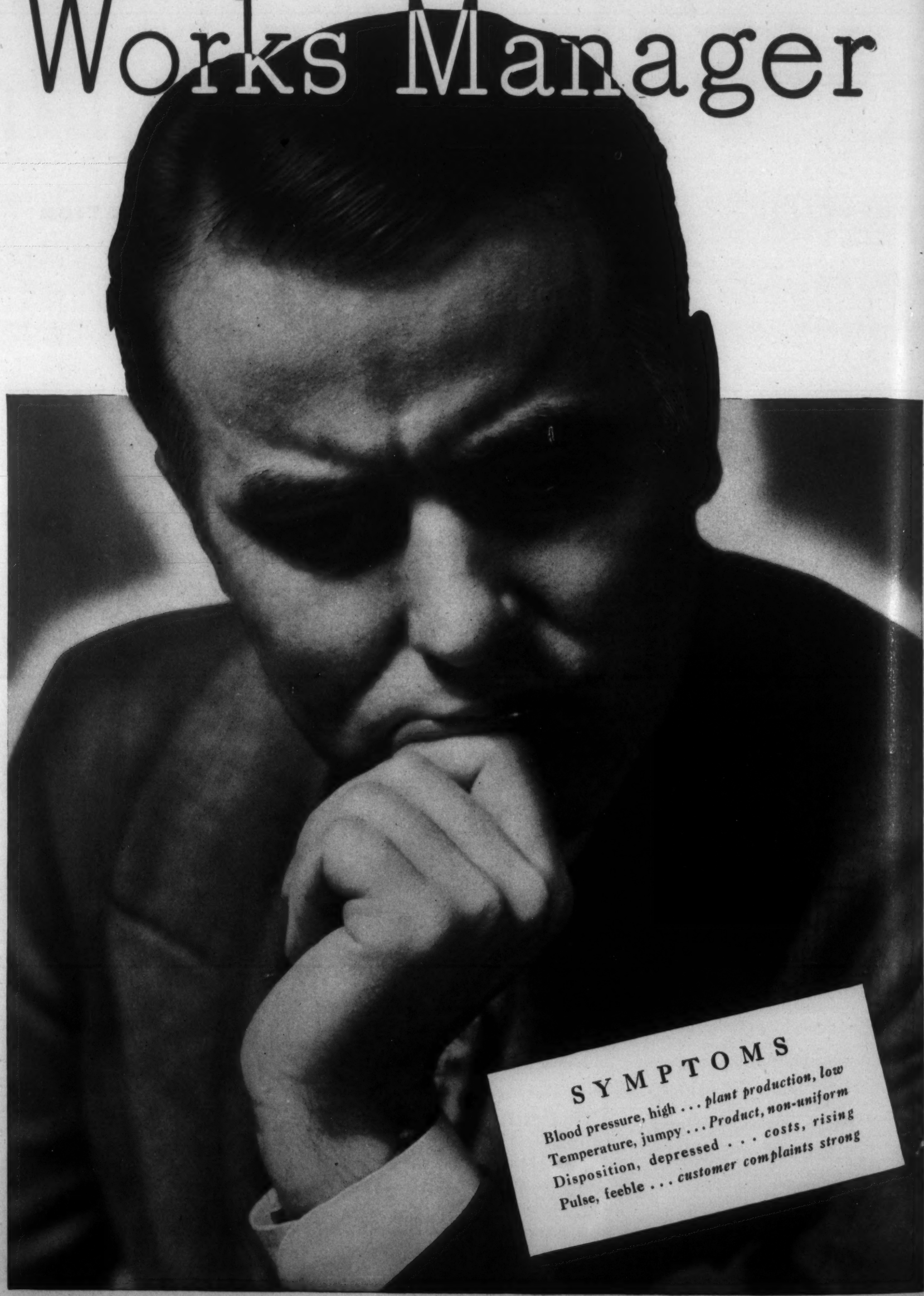
Annual Open-Hearth Conference . . . . . A 5

Highlights . . . . . A 21
Editorial . . . . . A 23
New Equipment and Materials . . . . . MA 262
Manufacturers' Literature . . . . . MA 267
Current News Items . . . . . MA 271
Book Reviews . . . . . MA 272

METALLURGICAL ABSTRACTS

Ore Concentration . . . . . MA 218
Ore Reduction . . . . . MA 219
Melting, Refining and Casting . . . . . MA 220
Working . . . . . MA 223
Heat Treatment . . . . . MA 224
Furnaces, Refractories and Fuels . . . . . MA 228
Joining . . . . . MA 233
Finishing . . . . . MA 236
Testing . . . . . MA 240
Metallography . . . . . MA 245
Properties of Metals and Alloys . . . . . MA 249
Effects of Temperature on Metals and Alloys . . . . MA 252
Corrosion and Wear . . . . . MA 254
Applications of Metals and Alloys . . . . . MA 256
General . . . . . MA 259

Works Manager


SYMPTOMS
Blood pressure, high . . . plant production, low
Temperature, jumpy . . . Product, non-uniform
Disposition, depressed . . . costs, rising
Pulse, feeble . . . customer complaints strong

THE DEVELOPMENT OF

A Slagging Test for Refractories

by Hobart M. Kraner

Development and Research Department, Bethlehem Steel Co., Bethlehem, Pa.

Fig. 1. Open-Hearth Door from Inside, Showing Erosion.

LIKE MOST OTHER COMMODITIES, refractories are subjected to two kinds of tests, (1) tests for purchasing requirements, and (2) tests for the ceramic technologist. The former are apt to be the more lenient, while the latter generally subject the materials to conditions which cause them to fail.

The interpretation of the values obtained may be based on the chemical analysis of the individual refractory constituents; the fineness or graduation of the grain sizing; the method of forming; the degree of pressure, plasticity, etc.; the manner, extent or temperature of firing; the atmosphere prevailing, whether oxidizing or reducing; and to some extent, the rate of cooling.

The ceramic technologist is most interested in knowing what has happened up to this point, while the consumer wants to know how the product will perform. In the former case, chemical analysis, porosity, fusion, density, crushing and rupture tests and petrographic studies generally indicate clearly what changes have taken place. These tests are fairly simple and the interpretation offers no particular difficulties.

To determine actual performance, however, is another story. This is not always easy, for the conditions under which these refractory materials are used may vary widely; several factors are generally involved which complicate matters so that no definite value of merit can be integrated from such data.

Intermittently operated furnaces impose severe penalties upon a refractory which does not stand the spalling action resulting from rapid heating and cooling; recent operating conditions have shown that furnaces where silica brick is used to best advantage during continuous operation may fail in intermittent operation due to spalling. Clay bricks, which are less refractory and have lower chemical resistance, but which are also less affected by temperature changes, replace silica to good advantage under such conditions.

By determining the physical properties of a refractory the ceramic engineer is able to form an opinion about its performance although he actually uses these data only as an aid in estimating the extent of slag penetration, the rate at

Fig. 2. Open-Hearth Door from Inside, Showing Drippage.

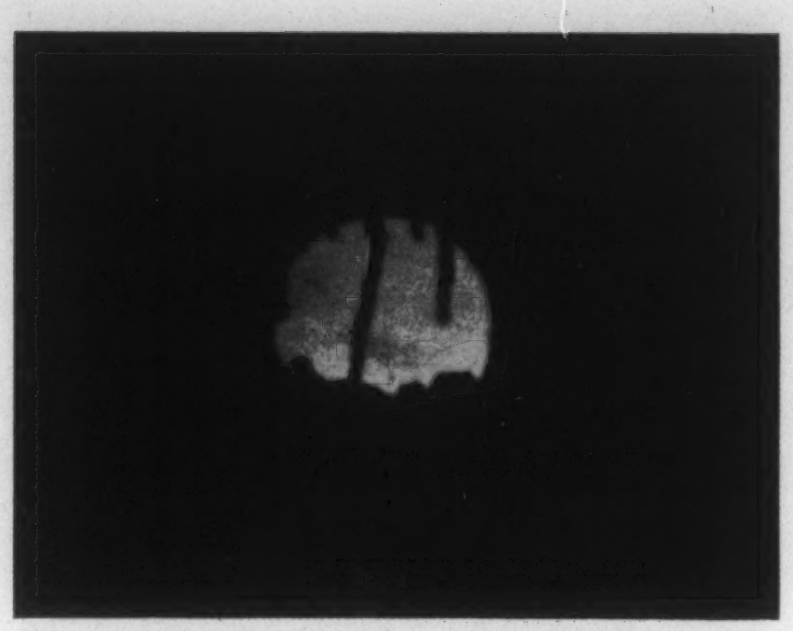


Fig. 3. View through an Open-Hearth Door Showing Corrosion Products of Clay Refractory.

which the bond will be broken down by the attacking slag, the probable reaction between slag and refractory mass as a whole, and the ability of the refractory to stand hot load and heat shock.

Tests Indicating Service Merit

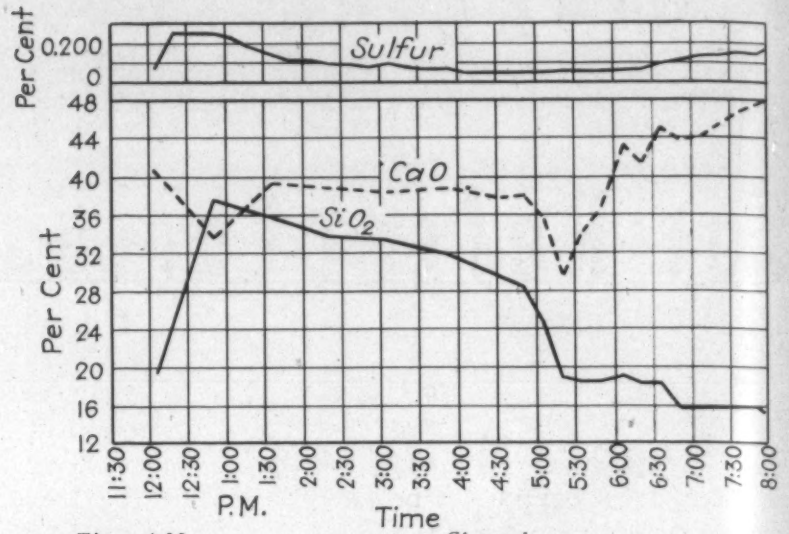
Fundamentally, from a consumer's point of view, there are three tests which largely indicate the service merit of a refractory: (1) Its ability to withstand heat shock, for which the panel spalling test has been developed, (2) the ability to withstand load at high temperatures, for which the hot load test has been developed, and (3) the ability to withstand chemical action, for which there is no generally accepted test. The reason for the industry having failed to standardize on one test probably lies in the fact that the conditions to be met are not clearly defined and because there has been some tendency to expect a single slag test to yield an answer to the merit of all refractories for all services. This, quite obviously, cannot be done.

There have been numerous attempts to develop such a test, but none have been universally adopted as a standard, because there is lack of coordinated consideration of the many applications for which such a slagging test must

Fig. 4. Corroded Face of an Open-Hearth Furnace Door.

serve, for instance, (a) boiler service, (b) glass tanks, (c) open-hearths, (d) chemical processes, (e) reheating (forge) furnaces, (f) metal ladles, (g) non-ferrous operations, etc. The temperatures and chemistry of each may be entirely different. It is conceivable that a mechanical procedure may be developed which can be used for all such tests, with variations in slag composition, temperature or temperature cycle to simulate the practice for which the test is being conducted.

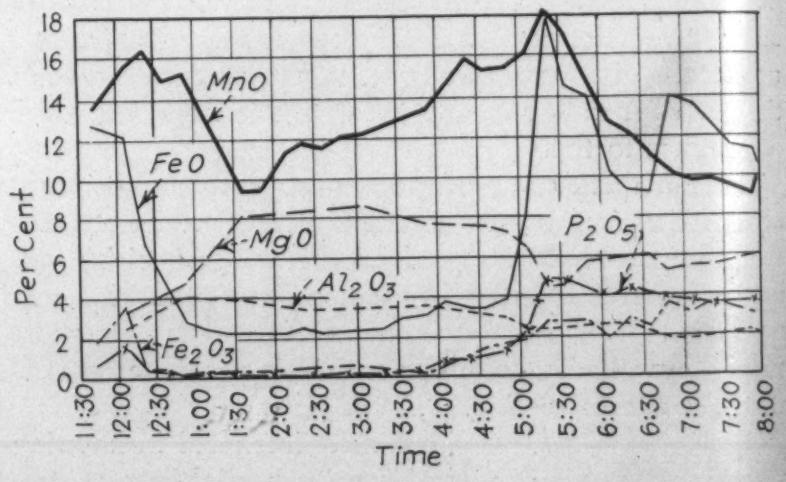
A systematic study of the conditions to be simulated must be made in order to determine the major factors involved, thus leading to some simplified practice. Supplementing



Time, A.M.	*Charged*
8:23-8:31	2,700 lb. dolomite on back wall
8:39-8:47	26,000 lb. limestone
8:52-9:01	1,570 lb. dolomite on front wall
9:06-9:20	175,000 lb. scrap

Fig. 5. Variation in Slag Composition from Hot Metal Addition to Tap.[20]

Fig. 6. Variation in Slag Composition from Hot Metal Addition to Tap.[20]



this, laboratory research revealing actual solubilities of refractory constituents in certain slags or fluxing compositions should assist in a fundamental way in deciding what constituents in slags or glasses are the most corrosive or dissolve the refractory to the greatest extent. Iron sulphide, iron oxides, lime and silica and combinations of these are those most frequently encountered by the steel maker, while the alkalies and lime are of most serious consequence to the glass man.

Consumption of Refractories

The importance of the problem is reflected by the great tonnages used. Tables 1 and 2 give reliable information on refractory consumption, by industries and in various applications.

Table 1.—Refractory Consumption by Industries[19]

Industry	Total Sales, Per Cent
Iron and steel	50.0
Public utilities	20.0
Non-ferrous metals	6.0
Cement and lime	5.0
Glass	5.0
Oil refinery	4.0
Cer. miscellaneous	3.0
Miscellaneous	3.0

Table 2.—Consumption of Refractories for 1926

	Total Per Cent	Percentage of Total: Clay Brick	Silica Brick	Other Refractories
Blast furnace and stoves	6.3	6.3	...	...
Open-hearth furnaces	34.1	12.1	21.0	1.0
Heating furnaces	7.3	6.8	0.5	0.01
Crucible furnaces	0.3	0.1	0.2	0.01
Electric furnaces	0.5	0.2	0.3	0.04
Cupola furnaces	2.3	2.3	...	...
Malleable furnaces	2.4	2.4	...	...
Bee hive coke ovens	0.9	0.6	0.3	...
By-product coke ovens	6.1	2.4	3.7	...
Smelting furnaces for copper, lead and zinc	2.9	1.8	1.0	0.10
Boiler furnaces	19.6	19.45	...	0.05
Gas generating plants	4.4	2.0	2.4	...
Chemical plants	1.0	1.0	...	...
Cement plants	1.9	1.8	...	0.10
Lime plants	1.7	1.5	0.2	...
Glass plants	3.1	2.1	1.0	...
Pottery and brick kilns	2.5	2.5	...	...
Miscellaneous	2.7	2.1	0.5	0.10

It is apparent that the steel industry, especially the open-hearth, consumes a large proportion of the refractories produced. The consumption is, to a very great extent, a chemical problem. Spalling, to be sure, is involved, but chemical action is reflected in the erosion and drippage such as can be seen in Figs. 1 and 2, typical illustrations of the fluxing action of oxides at high temperature. Frequently the spalling complication is a result of a slag penetration which produces a vitreous face, rigid at temperatures slightly lower than normal or constant operating temperatures; this vitreous slagged face is the real cause of spalling. Fig. 3 is a familiar sight to the open-hearth man and represents the refractory drip resulting from the continual wash of fresh slag on the hot inner face of a door. Fig. 4 shows the face of such a door and the worn refractory lining.

The Open-Hearth a Series of Processes

The open-hearth process is really a series of processes, so far as the conditions to be met by the refractories are

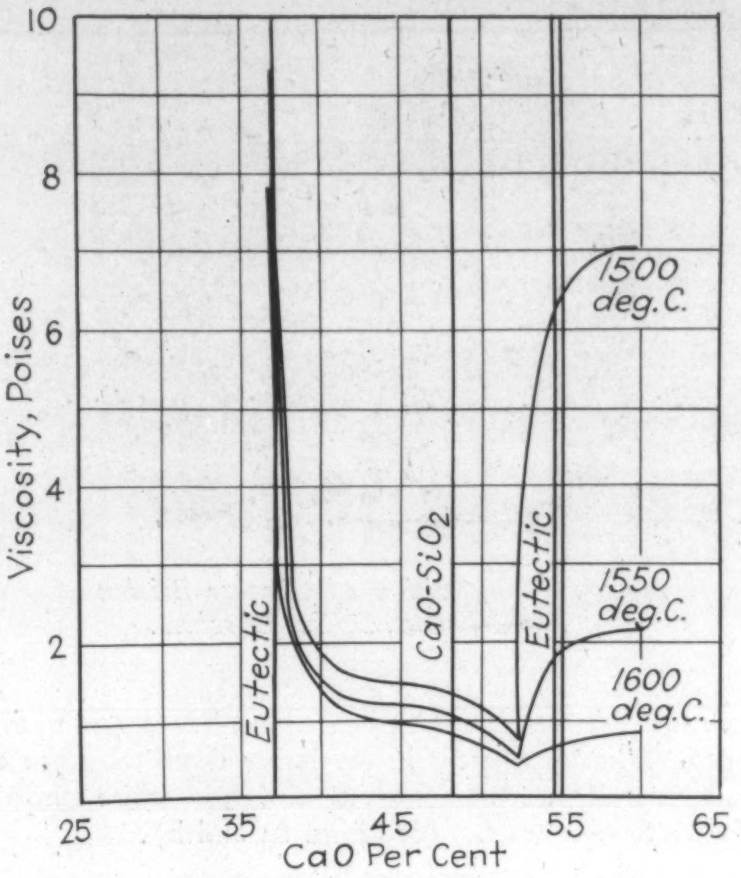


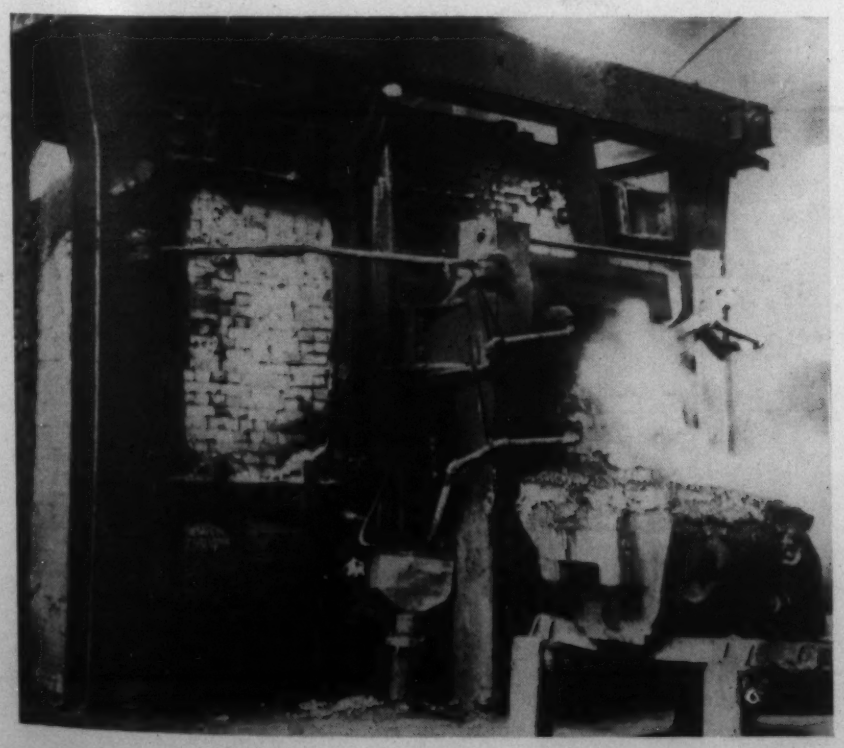
Fig. 7. Composition-Viscosity Relations in CaO-SiO_2 System.[21]

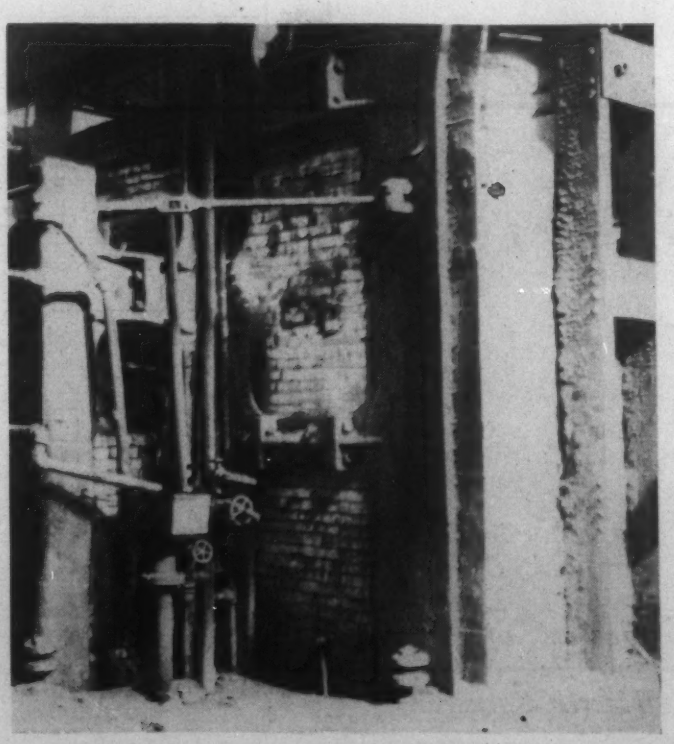
concerned. Slagging conditions do not only vary widely during one and the same heat, but there are also wide variations in temperature and slag characteristics from one heat to the next. Figs. 5 and 6 show the variations in the slag composition in a single heat.

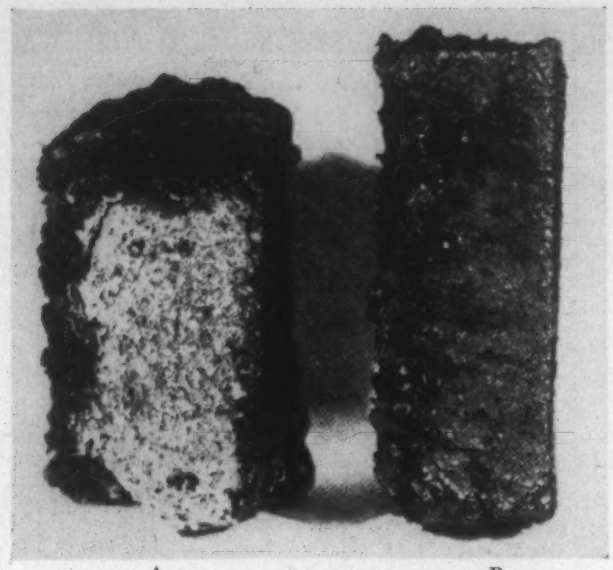
The refractories in contact with the slag are subjected to impingement by this slag and are, therefore, being constantly bombarded or washed by a fresh supply of corrosive material which, after exerting its solvent action, flows away with the products of solution, allowing a new face to be exposed.

In small open-hearths where the down-takes are necessarily of small dimensions, the severe erosion about 6 ft. above the floor level is due to the abrasive action of the solids as well as to the chemical action of the fluid slag. In

Fig. 8. a and b. Patching and Thin Wall in End Wall of Open-Hearth Furnace where Severe Corrosion Takes Place.







A B

Fig. 9. Composition of Checker Bricks; A, Air Checkers, B, Gas Checkers.

such small down-takes hot patches must be resorted to every 50 to 75 heats, whereas in the larger down-takes the end wall generally needs no patching during an entire campaign of 300 to 400 heats. (See Figs. 8a and b).

Effect of Reducing Conditions

While the open-hearth process is one in which oxidation is carried out, the gas uptakes are under reducing conditions at least half of the time. This results in a much shorter life of the end wall of a gas uptake than of the air uptakes. Both clay and silica bricks are more easily slagged under reducing conditions than under oxidizing conditions. Earl Smith[2] relates an instance where, under reducing conditions, one inch of the face of a silica roof was fluxed and melted in five minutes. The effect of this reducing condition in gas checkers is clearly evident from Table 3. The dust has had an opportunity to oxidize while the furnace was cooling, whereas the dust which penetrated the brick had no chance to oxidize. The conditions which apparently did not cause severe corrosion of the checker brick in Fig. 9 are sufficiently severe in the end wall portion of the gas uptake to give the shorter life referred to previously.

Table 3.—Analysis of Air and Gas Checker Deposits, Percent, According to Whitely and Hallimond[22]

	Dust from		Brick from	
Constituent	Air checker	Gas checker	Air checker	Gas checker
SiO_2	3.0	4.1	71.8	71.6
Fe_2O_3	95.9	94.1	26.1	3.7
FeO	...	...	0.3	22.9
Al_2O_3	0.4	0.45	...	...
MnO	0.4	0.35	...	...
CaO	0.05	0.4	...	...

The dust in the checkers (Fig. 10) has little to do with the slagging of checker bricks, except when the combustion conditions get out of control temporarily and flames enter the checkers and melt these deposits. This may be an occasional occurrence or, as is usually the case, the furnace may be operated far beyond its designed rating. In the latter case, serious fluxing or glazing of the upper layers of the checker setting is the result. The glazing and sticking together of these bricks means a low recovery during a furnace rebuild due to breakage in removal. No improvement of the refractory will change this condition, for it is largely a case of melted deposit rather than a fluxed refractory which causes the glazing, sticking together, and the consequent high consumption of checker bricks. The remedy in such a case is to redesign the checkers, slag pockets, and down-takes, but this, in many instances, cannot be done because of lack of space. The larger furnaces use practically no new checker bricks in rebuilds because there is no sticking together from these fluxed deposits.

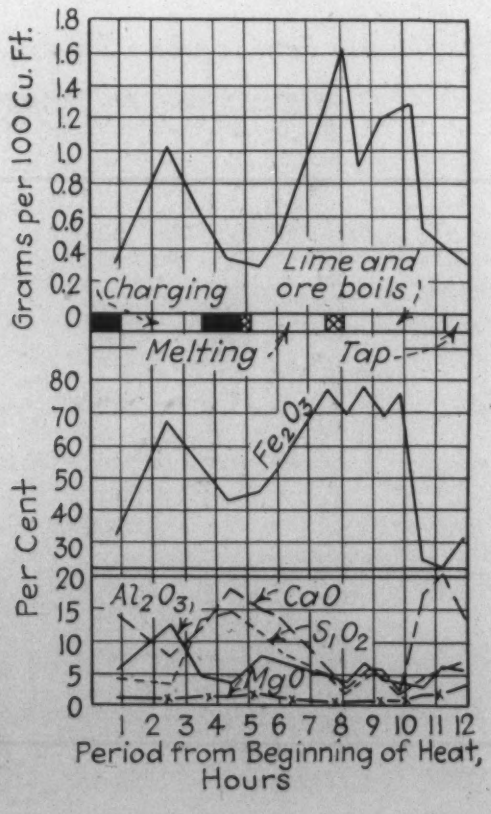


Fig. 10. Concentration and Composition of Dust in Checkers of a 50-ton Basic Open-Hearth Furnace.[22]

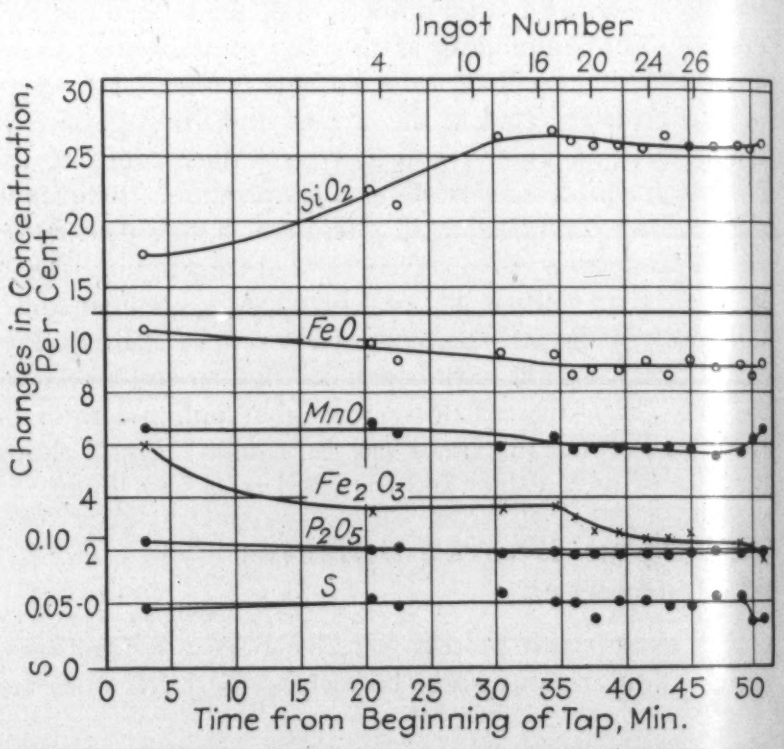


Fig. 11. Changes in Concentration of Slag Constituents.[21]

Effect on Ladle Linings

Ladle linings slough away at the rate of ½ to ¾ of a brick per ton of steel. This goes into the slag, changing its composition as shown by Fig. 11 and Table 4.

Fig. 12 indicates that at the end of a ladle lining life, the wear opposite the pouring spout (Section A-a) is caused by impingement of metal. The wear around the bottom of the ladle wall may be caused by the formation of oxide due to the splash when the ladle is being filled. It

Table 4.—Comparison of Tapping and Ladle Slag[20]

	Final Slag	Ladle Slag
P_2O_5	3.66	2.82
SiO_2	15.58	23.58
FeO	10.70	9.64
Fe_2O_3	3.28	0.93
MnO	9.74	10.14
CaO	48.00	39.60
MgO	6.02	5.30
S	0.163	0.110
Al_2O_3	2.08	6.25

may be more logically attributed to the longer exposure to the high temperature, for the lower portion of the ladle is the first to receive the hot metal and the last to be relieved of it. By the time the slag reaches the lower portion of the ladle, it has already dissolved considerable lining; from a solubility standpoint, it should, therefore, not be expected to be seriously corrosive to the lining. Only by reason of the high temperature of the ladle lining is this so. This same action is noted in the stopper refractories. Neither is really refractory, but they are fairly impervious to the penetration of slag. Because they operate at their fusion point they are readily soluble in the slag at this high temperature.

Numerous methods for testing slag are available, as may be seen from the accompanying bibliography. However, the problem to develop a test, the mechanics of which is universal or nearly universal, and to find through laboratory research how many slag compositions should be used in such simulative tests, will require more time than any writer has had to devote to this important subject.

The foregoing discussion is meant only to point out the considerations which must be kept in mind in the development of the mechanical portion of such a test. Obviously,

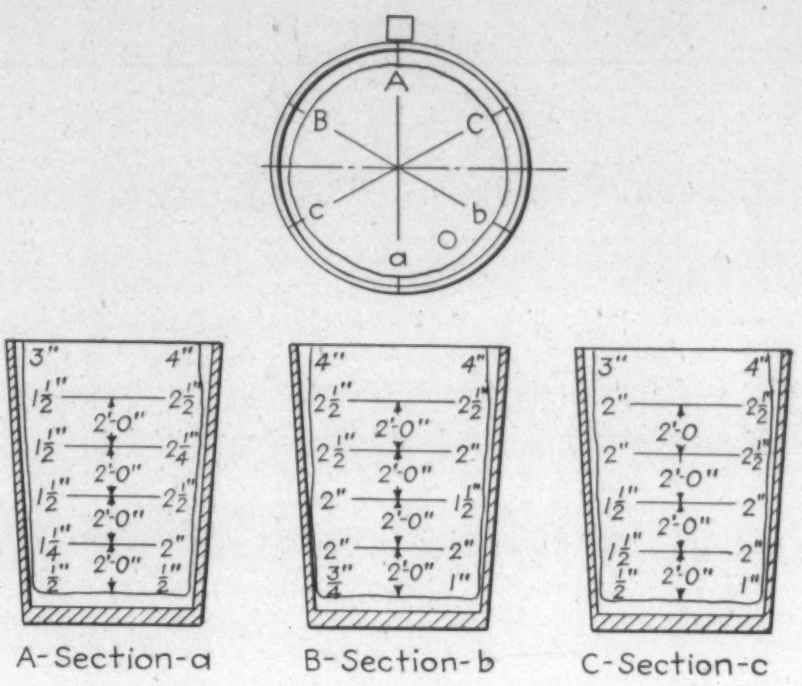


Fig. 12. Diagrammatic Illustration of Erosion of Ladle Lining.

in such a test the following conditions must be carefully controlled:

(a) Temperature or temperature cycle involved and its uniform application to all test pieces.
(b) Atmospheric uniformity (oxidizing or reducing).
(c) Proper slag composition.
(d) Viscosity of slag during the entire test.
(e) Rate of slag application and drainage.
(f) Rate of flow of combustion gases past the test speciment during the test.

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Courtesy: Ford Motor Co.

Pouring Open-Hearth Steel Ingots

SEVENTH REPORT ON THE

Heterogeneity of Steel Ingots

—AN EXTENDED ABSTRACT

by Fred P. Peters

Assistant Editor, METALS AND ALLOYS.

This is the first part of an extended abstract of the Iron and Steel Institute's Seventh Report on the Heterogeneity of Steel Ingots, and covers those sections of the report that deal with internal evidences of uneven distribution of constituents and inclusions. The large part of the report that deals with methods and equipment for determining oxygen in steel will not be abstracted. The concluding installment, to be published in a later issue, will discuss an important external factor, the ingot mold.

ANY CONSIDERATION OF THE MECHANISM of freezing of steel ingots necessitates discussion of killed ingots as a class apart from semi-killed and rimming steel, not because there is a fundamental difference in the physical laws involved, but because the liberation of gases in unkilled steel introduces a complicating factor. In its introduction to the Report, the Heterogeneity Committee reviews our current knowledge on the freezing of killed ingots as a preliminary to Swinden's brief and clear study of composition variations in rimming steel.

The Freezing of Killed Ingots

Although there is still much to be learned and many controversial issues to be settled concerning the freezing of killed ingots, previous reports of the Committee and others have indicated general agreement on the following points:

The first stage in freezing is the formation of the outermost, or "chill" skin, a region composed of extremely minute crystals, not microstructurally resolvable. Inside this is a zone of columnar crystals, which grow not exactly normal, but at a slight upward inclination, to the surface. Inside this columnar zone is the region of equiaxed grains. At present the great number of variables does not permit control of the position of the columnar-equiaxed interface, for some (austenitic) steels have been observed to be entirely columnar, whereas others have been entirely equiaxed. The grains in the columnar zone grow dendritically, and this zone, when it differs at all in composition from the rest, contains slightly more than the average C, S and P.

The lower central portion of the equiaxed zone is of higher purity than the average of the ingot. The average composition is fairly well represented by the central portion of the ingot about half way between the top and bottom. This "purer" zone is bounded by the inverted Vee segregates, long parallel strings of high C, S and P material, more numerous at the top than at the bottom.

The Committee still holds differential freezing to be the primary cause of heterogeneity in killed ingots. Thus C, S and P, whose respective binary systems with Fe possess the greatest solidus-liquidus ranges, show the widest segregation, while Si, Mn, Ni and Cu show the least. Segregation varies with ingot size, for greater size means slower cooling and more extensive differential solidification. That the rate of cooling is a dominant factor is indicated by the fact that in small ingots slow cooling has produced greater segregation than ordinary rates.

The reasons for the existence of the "purest" zone are still elusive. The balance of probability seems to be in favor of the central pure zone being due to the movement of impurities away from it, rather than to the falling into it of a shower of pure crystallites (around non-metallic nuclei), as has been suggested by some. Precise knowledge of diffusion or mechanical motion in the interior of the ingot is still lacking and, therefore, it is impossible to derive a completely acceptable explanation for the concentration of soluble and insoluble impurities in the upper portion of the ingot, or for the exact manner in which the inverted Vee segregate forms, or for the critical factors that determine whether and where crystallization will be columnar or equiaxed.

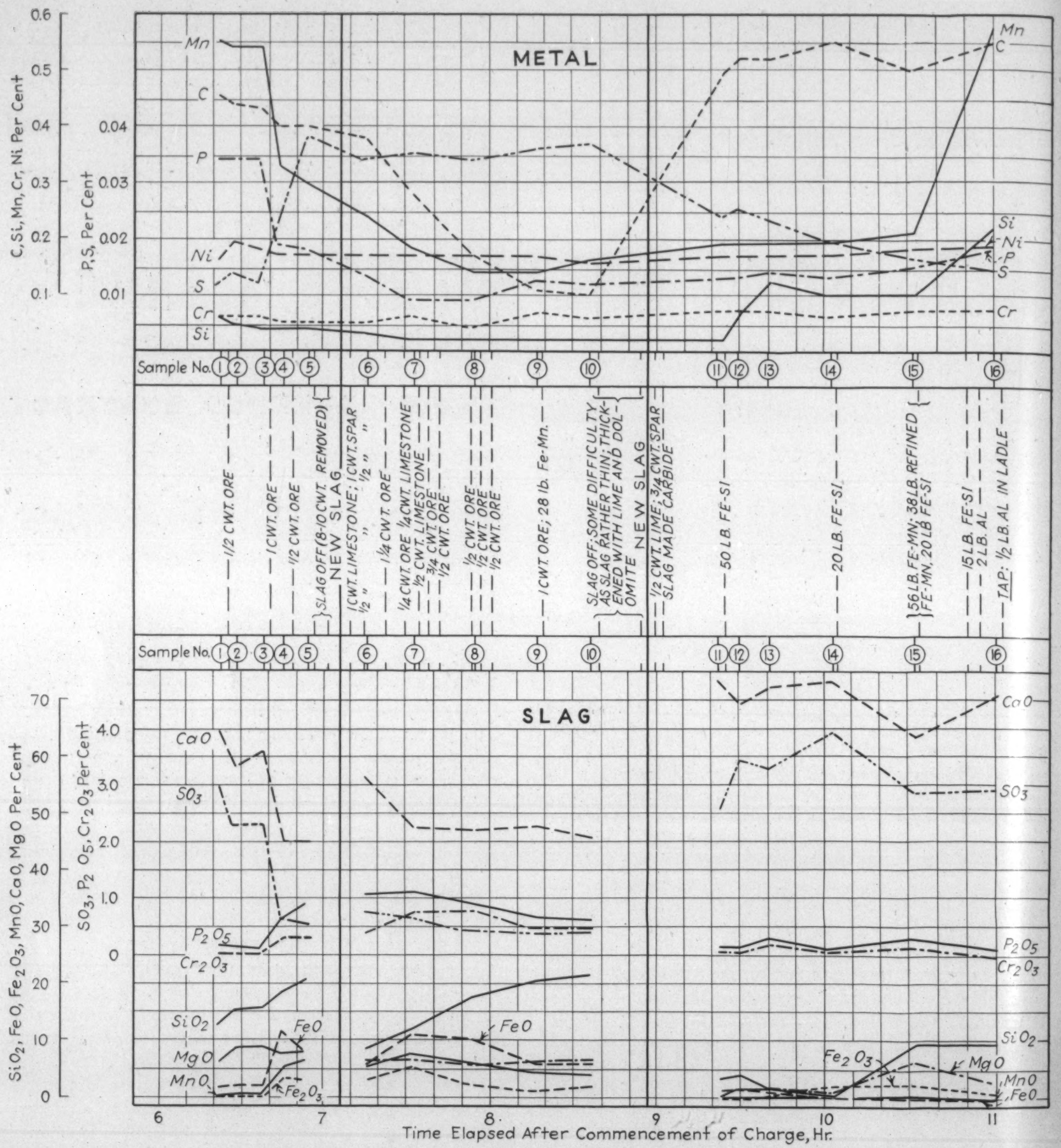


Fig. 1. Variation in Composition of Metal and of Slag during Progress of the Heat.

Rimming Steel

The general characteristics of rimming steel ingots are referred to many times in the Committees' Reports. It is well known that a fully rimmed ingot possesses an outer rim that is lower in C, S and P than the average composition of the steel, and a core that is higher than the average. Swinden's contribution[1] to the present Report adds new data on the distribution of the "impurities" in a relatively high C, 3 in. open-hearth rimming steel billet and in a 24 in. basic Bessemer ingot. His study was made not only to observe the characteristics of the material, but to furnish a basis for explanation of the rimming phenomenon. In this abstract, Swinden's data on the 3-in. billet will be omitted, for the results were similar to those obtained on the 24-in. ingot and the latter has the advantage of being more representative of production conditions.

The average analysis, as made on samples from the melt, was:

	24 in. B. B. Ingot, Per Cent
Carbon	0.06
Manganese	0.54
Silicon	0.005
Sulphur	0.026
Phosphorus	0.048

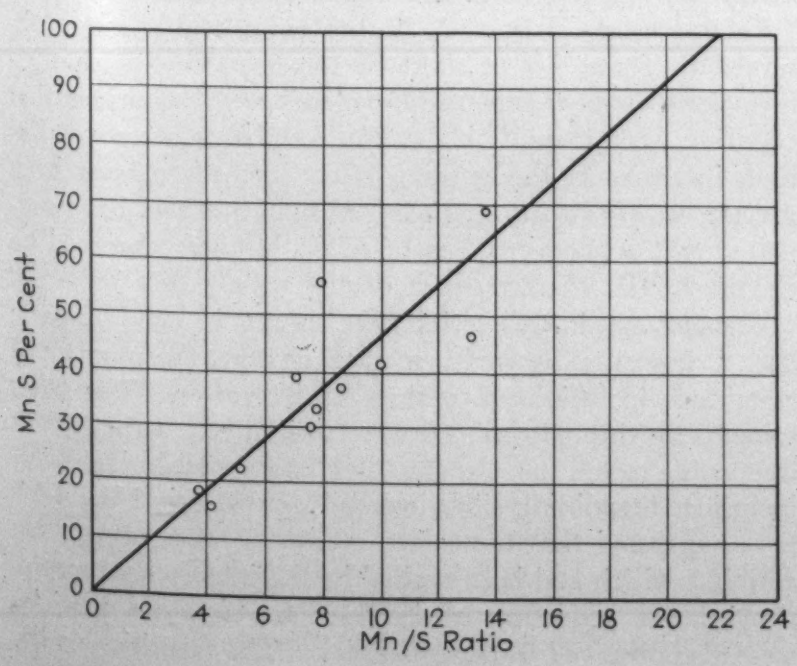
Samples were taken at intervals of 1/32 in. from the sur-

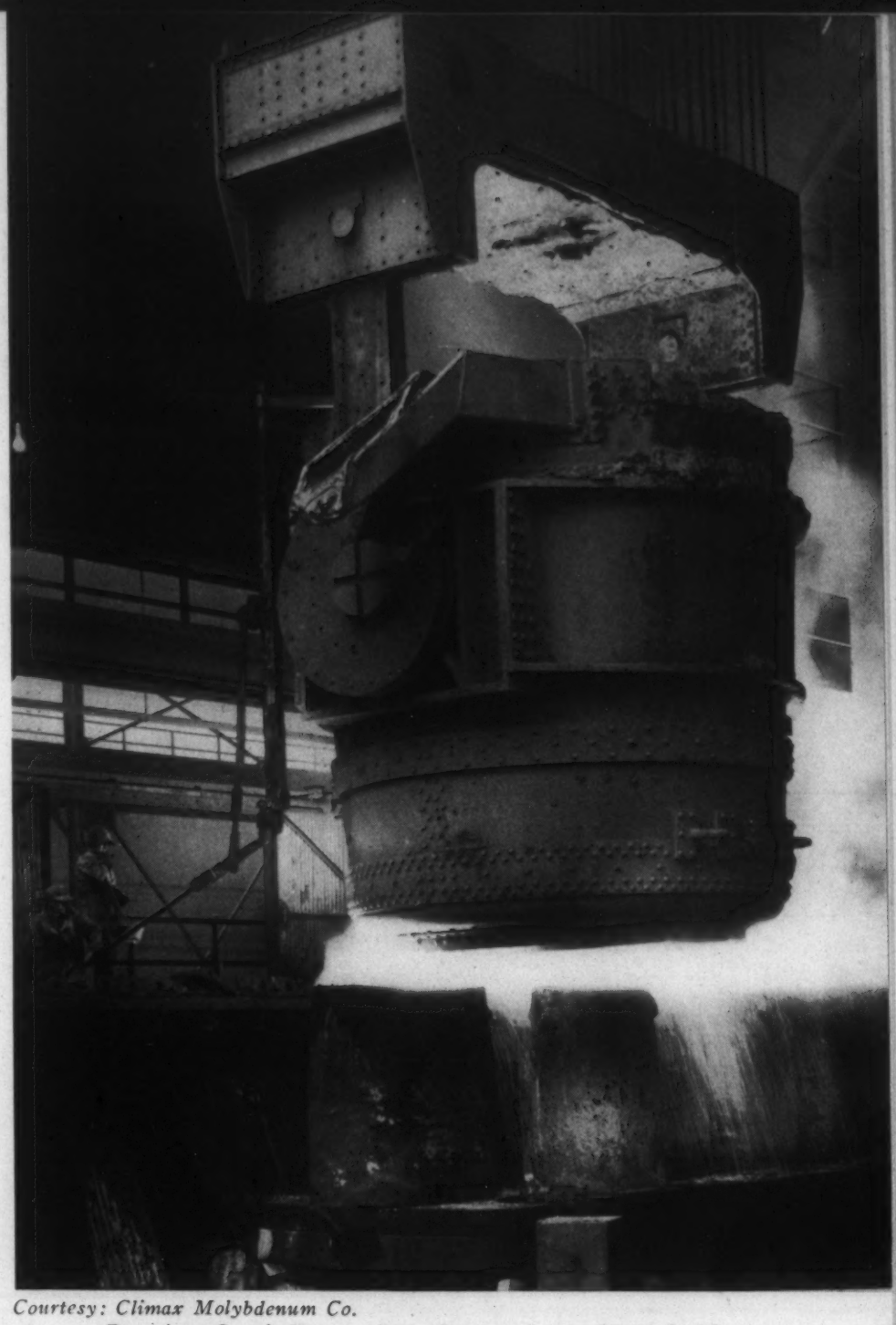
face to the center and analyzed for C, S, P and Mn. The total range of C variation was very small, as might be expected with an average C content of 0.06 per cent, but it did include a slight fall from 0.063 per cent at the edge to 0.04 per cent close to the rim-core junction, then a sharp rise to a peak of 0.08 per cent and an irregular, slight drop to 0.07 per cent at the center. Sulphur dropped from 0.027 to 0.015 per cent through the rim, rose to a peak of 0.055 per cent at the junction, then flattened towards the center, with, however, a decided secondary peak to 0.05 per cent along the way. The P trend was very similar, dropping from 0.04 to 0.03 per cent, then rising to a peak of 0.08 per cent at the junction, and finally flattening quickly to 0.065 at the center; P content also showed a secondary peak, coincident with the S.

The variation in Mn content was similar to that of the other constituents through the rim, dropping from 0.55 to 0.51 per cent; at the junction the Mn rose to 0.57 per cent, but unlike the others, did not fall on continuing to the center. Swinden points out that the changes in Mn content cannot be correlated with the S variation to postulate combination as pure MnS.

The work is now being extended to include oxygen determinations through a similar zone of the same ingot, which are essential to the establishment of an acceptable hypothesis for the "rimming phenomenon." Swinden suggests that the initial progressive reduction of C content through the rim is due to the reaction between the C and the FeO, this reaction ceasing (and the C content jumping to a peak) when the FeO content at the existing temperature falls below that necessary to enable the reaction to proceed in a positive direction. The peaks at the core-rim junction may be accentuated by the "collection" of segregates around the blow-holes. Also, a proportion of the more fusible constituents (carbides, sulphides, phosphides) are apparently carried forward by the advancing wall of the rim. When these reach the neighborhood of the core, their continued free movement is possibly prevented by the changed solidification process (reduced temperature gradient) and they tend to pile up at the junction. Finally, the streamer segregates observed rising upwards and inwards inside the junction may be responsible for the pronounced secondary peaks in the S and P contents.

Fig. 2. Relation of MnS Content to the Mn/S Ratio





Courtesy: Climax Molybdenum Co.

Pouring Steel Ingots in a Large Open-Hearth Plant.

Inclusions Present at Different Stages of Melting

The changes in the nature and amount of inclusions as a heat of basic electric furnace steel was carried through its progressive stages were carefully determined by Whitely.[2] In making his tests, Whitely took samples in duplicate, in each case allowing one sample to solidify undisturbed, and killing the other in the spoon with aluminum. His results are particularly interesting, not only because of this careful consideration of the effect of sampling procedure, but also because he shows that much of the sulphur in ordinary steel solidifies as iron sulphide, which changes later to manganese sulphide in the solid steel.

The melt was prepared in a 9-ton 3-phase Heroult arc furnace. The charge consisted of 17,600 lbs. of carbon steel scrap of known analysis to which were added 40 lbs. of crushed electrode carbon. The various stages of melting at which samples were drawn, and the progressive variation in metal and slag analyses are given in Fig. 1.

All samples were taken in duplicate from as nearly as possible the same position in the furnace and as nearly simultaneously as possible. One series (Series I) were allowed to cool in the spoon under the slag, while the other (Series II) were skimmed at once, killed with a known weight of aluminum wire and poured into a shallow mold.

A counting method was adopted for determining the relative amount of inclusions of different types present in the various samples of Series I. The results of the inclusion count are given in Table I.

Table I—Results of Inclusion Count. Figures are average number per 1/25 sq. in. of area.

	Series I					Series II
Sample Number	Stage of Process	Number of Counts	SiO_2 and Silicates, Average	Sulphides, Oxides, Average	2% HCl in Alcohol. % Sulphides Attacked *	Sulphides Average
1	First Oxidizing	30	10	22	..	47
2	"	20	18	27	..	41
3	"	30	16	28	..	37
4	"	20	42	35	..	..
5	"	30	45	25	5	..
6	Second Oxidizing	20	4	41	8	..
7	"	20	..	38	15	..
8	"	20	..	46	45	..
9	"	30	..	60	40	..
10	"	20	..	49	77	..
11	Refining	20	25	39	10	65
12	"	30	28	29	5	65
13	"	30	26	45	2	..
14	"	20	20	27	Nil	55
15	"	20	23	24	Nil	..
16	"	20	10	22	..	..
17	"	20	8	22	..	..

* The figures in this column are the percentage of sulphide inclusions that also contained FeO.

Nature of Inclusions

The original paper included 76 photomicrographs, showing typical distribution and appearance of the inclusions. Series I contained (1) sulphides, (2) silica globules and silicates, (3) oxides of iron and manganese, and (4) slag particles. In the inclusion counts reported in Table I, sulphides and oxides have been counted together, because the two forms were invariably associated.

In Series I the sulphides occurred in two forms, the yellow, brittle iron sulphide and the dove-gray sulphide commonly referred to as manganese sulphide. In the first 4 samples FeS was not observed, but it began to appear as the Mn content dropped. When both MnS and FeS were present in the same inclusion, the demarkation between them was very sharp. Some MnS was seen in all the samples low in Mn, and in Nos. 16 and 17 it was the only sulphide present.

The oxides present in the Series I samples were called FeO, although probably a little Fe_3O_4 and some MnO were always present. The occurrence of the characteristic FeO-FeS eutectic in the FeS inclusions is a sure indication of the presence of oxygen in the metal; it was frequently observed in samples from the second oxidizing period. Carefully made tests also showed that a considerable amount of MnO in the FeO inclusions did not interfere at all with the detection of oxides by the 2 per cent HCl solution used for this purpose.

The silica and silicates observed in Series I existed as minute globules that varied in transparency from clear glass to opaque. They vary in color apparently according to the degree of deoxidation of the steel; small quantities of FeO are sufficient to stain them dark red, and larger amounts render them opaque. The color of these inclusions is therefore a qualitative indication of the state of the bath.

The distribution of both silica and silicate inclusions was fairly uniform. In the first oxidizing period of Series I they were frequently associated with MnS. Often the silicate completely enveloped the MnS, but sometimes the latter was divided by silicate veins. No definite instance was observed in which FeS was a constituent of these composite particles, the sulphide having always in such cases the dove-gray color of MnS.

Discussion—Series I (Unkilled)

Examination of Fig. 1 will show the 3 distinct stages in the history of the melt: (1) an oxidizing period prior to the removal of the melting slag; (2) a second oxidizing period following the preparation of a new oxidizing slag; and (3) a refining period after introduction of a carbide slag. The three stages in melting are clearly discernible in the variations in inclusion contents given in Table I. In the first oxidizing period the number of silica and silicate globules increased; towards the end, FeS first appeared owing to a sudden rise in the oxidizing power of the slag.

The second stage, in which a good boil was maintained, was marked by a sudden drop in the number of silica and silicate inclusions, and the appearance of large amounts of FeO. The FeO-FeS eutectic was abundantly present in samples 8 and 9. No eutectic of MnS and FeO was ever visible, composite inclusions containing both showing clear separation. The last sample in this period showed the greatest MnS and FeO, invariably together. All samples from this stage revealed marked segregation; sulphide inclusions, with FeS preponderating, were very numerous.

The third stage of the melting process was characterized by the reappearance of silica and silicate globules and by the eventual disappearance of visible FeO. No samples later than No. 11 showed the FeO-FeS eutectic; in samples 14-17 even the FeO film at the boundaries of FeS particles had vanished. Thus, the gradual increase of undissolved FeO in the first and second periods and its rapid elimination in the third could be followed. An interesting effect was that of the added Al (in samples 16 and 17), on the appearance of the MnS, which in these samples occurred chiefly as fine particles or tiny broken films at the grain boundaries, rather than as the customary larger globules. As the third stage progressed, gradual replacement of the silicates by silica was observed; the latter was surprisingly abundant, even in sample No. 17, which represented bath conditions after a 90 min. refining period.

Series II (Killed)

Samples in this series were solid, unsegregated and practically free of slag. Aluminous inclusions had replaced FeO and most, if not all, of the silica and silicates observed in Series I. In most of the samples the alumina inclusions were so fine and so mixed with sulphides that counting was inapplicable. The sulphides were smaller than in Series I; the refining effect seemed to have been greater on MnS than on FeS. Although others have suggested that Al converts FeS to Al_2S_3, Whitely observed no change in the characteristics of the yellow FeS.

Samples 1-3 in this series were similar in every respect; No. 4, however, showed a marked change, the number of aluminous inclusions becoming much greater. The other samples up through No. 10 were so like No. 4 that it was impossible to tell them apart. FeS and a vitreous spherical inclusion, resembling silica, were also present in Nos. 4-10. It is suggested that these last inclusions were transparent alumina, which had been melted by the intense heat accompanying the reduction of FeO. Some free Al particles were also observed in these samples. The transition to the

third stage in Series II was indicated, in sample No. 11, by the complete disappearance of the clustered Al_2O_3 particles previously so prominent. Some glassy inclusions, consisting of Al_2O_3 and Al_2O_3 plus SiO_2, were observed. The FeS and MnS present in this last period became progressively less associated with Al_2O_3, indicating a steady elimination of oxygen during this refining period.

A small but rich segregate was observed in many of the samples in both series, but particularly in Nos. 1-3 of Series I, which gave all the etching reactions of free cementite. This segregate occurred less frequently as the C and Mn contents of the bath began to drop, disappeared from samples 7-10, and reappeared (but not immediately) after the introduction of the carburizing slag present in the refining period. It is impossible to explain the formation of this massive carbide, if such it be, on the basis of the iron-carbon diagram, and its nature must therefore be further investigated.

Because Series I samples contained such a large amount of slag particles and of FeO apparently formed *during* the sampling procedure, specimens obtained as in Series II by skimming and killing with Al, are believed to be more reliable for the determination of "oxygen contents" of steel baths.

A Note on Sulphides

MnS and FeS were often associated as a single inclusion, in which the boundary line between the two constituents was sharply defined. The MnS phase of these composites was unlike many of the inclusions that consisted entirely of MnS, being lighter in color and less translucent than the latter. It is believed that the "off-color" MnS contains dissolved FeS.

From careful sulphide inclusion counts data were obtained on the relation between MnS content and Mn/S ratio in the bath, which are plotted in Fig. 2. The relation is seen to be linear; in addition, the extrapolation shows that a Mn/S ratio of 22 was necessary to give MnS inclusions not discolored by dissolved FeS. However, in ordinary steels, the lowest ratio plotted (3.9) is usually sufficient to insure the absence of FeS in the finished product. Apparently the samples used in the present work were cooled too rapidly to permit the customary reaction to proceed to equilibrium. This the author checked by heating other sections of his samples for long periods at 1200 deg. C.; subsequent examination failed to disclose any FeS.

Thus, because samples cooled very rapidly from the liquid state show FeS and those allowed to cool more slowly do not, Whitely concludes that the reaction

$$FeS + Mn = MnS + Fe$$

generally occurs in the solid steel and proceeds so to completion. Following this line of thought, he cooled samples of 0.60 Mn, 0.06 S steel from the liquid state at different rates and observed FeS even in small ladle samples cooled to 900 deg. C. in less than 1 min. The evidence given in the paper is conclusive that at least part of the sulphide solidifies as FeS in ordinary steels in which it is certain that only MnS would appear in the finished product.

This new conception of the formation of some solid FeS in high-Mn steels and its reaction with Mn in the solidified steel also successfully explains the frequently observed deficiency of extra Mn in segregated zones high in MnS.

Courtesy: Climax Molybdenum Co.

Open-Hearth Steel Being Poured into Ingot Molds

Direct Oxide Determinations

Using the same series of samples employed by Whitely, Raine and Vickers[3] determined by chemical analysis the amounts of oxides of Si, Fe, Mn, Al present. Both the alcoholic iodine and the vacuum fusion methods were employed. The results obtained checked the inclusion counts reported by Whitely very well. Also, remarkably close agreement was obtained between the total oxygen content calculated from the results of the alcoholic iodine extractions, and the total oxygen determined by the vacuum fusion method.

Table II—Lower Oxides Expressed as a Percentage of the Steel.

Sample Number	Alcoholic Iodine Extraction					Vacuum Fusion
	SiO_2	FeO	MnO	Al_2O_3	Calculated Oxygen	Oxygen
1	0.009	0.024	0.0073	0.016	0.0193	0.019
2	0.009	0.022	0.016	0.014	0.0199	0.0196
3	0.009	0.025	0.016	0.013	0.0202	0.0208
4	0.016	0.029	0.033	0.009	0.0264	0.0258
5	0.016	0.042	0.026	0.009	0.0279	0.027
6	0.006	0.044	0.009	0.008	0.0188	0.020
7	0.006	0.055	0.0073	0.007	0.0204	0.022
8	0.007	0.086	0.008	0.007	0.0279	0.029
9	0.007	0.077	0.008	0.008	0.0263	0.026
10	0.007	0.075	0.009	0.007	0.0257	0.0245
11	0.012	0.038	0.010	0.008	0.0208	0.022
12	0.016	0.035	0.009	0.008	0.0221	0.022
13	0.019	0.028	0.008	0.008	0.0219	0.021
14	0.016	0.023	0.0073	0.009	0.0193	0.018
15	0.011	0.017	0.0054	0.010	0.0157	0.015
16	0.009	0.010	0.0036	0.013	0.0140	0.013
17	0.010	0.008	0.0027	0.016	0.0150	0.0129

Table II gives the results of the extraction [calculated to *lower* oxides of Fe and Mn], the "calculated oxygen" and the oxygen determined directly by vacuum fusion.

(Continued on page 93)

LABORATORY INVESTIGATION OF

Low Temperature Impact Properties

OF SOME S.A.E. STEELS

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THIS INVESTIGATION was inaugurated to obtain sub-zero impact strengths of a carbon-molybdenum steel and several of the more common SAE steels. In particular, it was desired to know what steels could meet an arbitrary minimum Charpy impact strength of 10 ft. lbs., when tested at low temperatures encountered in service. A review of available literature disclosed that published information was notably deficient and, in some cases, of questionable value because of failure to standardize or control testing conditions.

Experimental Procedure and Preparation of Test Specimens

Due to the greater rapidity with which a Charpy bar can be transferred from the cooling bath to the impact testing machine and fractured, it was decided to use the Charpy specimen rather than the standard Izod bar.

The 45-deg. V-notch Charpy impact specimen, machined to the dimensions given in Fig. 1a, page 1510 of the American Society for Testing Materials' 1937 Tentative Standards was used throughout the present investigation. Recently, considerable low temperature impact testing has been done, using a Charpy bar with the keyhole notch described in the National Metals Handbook. It is regrettable that the importance of low temperature impact testing has not been recognized by official designation of a standard test specimen, thereby making possible a direct comparison of results obtained by different laboratories.

All specimens were broken on a 40-mm. span in a pendulum type impact machine rated at 120 ft. lbs. The weight of the hammer was 23.571 lbs.; the length of the pendulum (measured from the axis of rotation to the point of contact with the specimen) was 31.497 in. The hammer was released from a point 20 deg. off the vertical position, swinging through an angle of 160 deg. before striking the specimen. The velocity of the hammer at the moment of impact was calculated to be 18 ft. per sec.

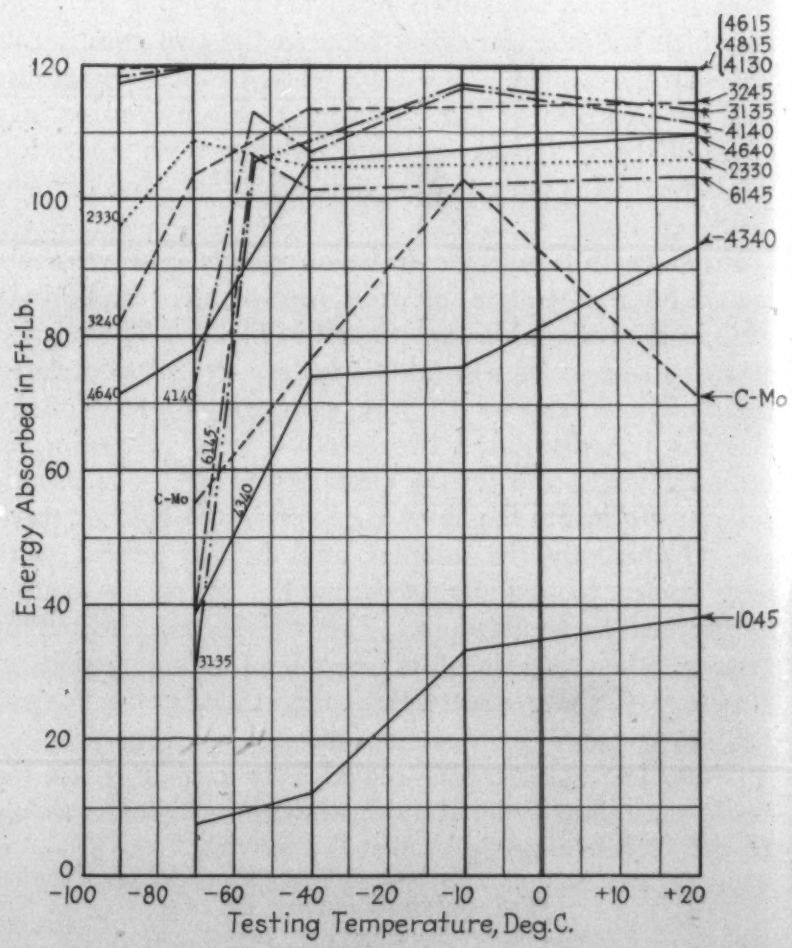

Fig. 1. Average Impact Properties of SAE Steels at Indicated Temperatures.

For temperatures down to —70 deg. C., the cooling medium was a mixture of alcohol and solid CO_2. A solution of liquid air, alcohol, and solid CO_2 was used to obtain the temperature of —90 deg. C. while —190 deg. C. was made possible by the use of liquid air alone.

The test specimens were held at the sub-zero temperatures for ½ hr. before testing. Between one and two seconds elapsed from the time the specimen was removed

Table 1.—Average Impact Properties of Several SAE Steels Normalized at Indicated Temperatures

Heat Treatment and Hardness				Energy Absorbed in Ft. Lbs. at Indicated Temperatures					
SAE No.	Normalized	BHN	Grain Size	BHN	—70° C. or —94° F.	—40° C. or —40° F.	—10° C. or +14° F.	+20° C. or +68° F.	+95° C. or +203° F.
4130	1650	235	8	235	(5)† 7.4	(6) 9.5	(3) 18.9	(2) 23.5	(3) 108.4
4140	1650	255	8	255	(6) 4.9	(6) 6.1	(3) 9.0	(3) 18.4	(3) 41.7
4615	1630	192	7-8	192	(6) 14.9	(6) 28.3	(6) 54.2	(3) 100.1	....
4640	1700	235	8	235	(6) 6.5	(6) 9.6	(3) 15.3	(3) 25.5	(3) 93.8
4815	1700	202	8	202	(6) 18.2	(6) 31.4	(5) 68.6	(3) 86.4	....
4340	1630	440	8	440	(6) 4.8	(6) 6.6	(3) 7.5	(3) 12.4	(3) 14.3
C-Mo*	1700	137	3-8 Duplex	137	(6) 4.8	(6) 8.8	(6) 40.5	(3) 84.3	....
2330	1675	192	7	192	(6) 9.3	(6) 17.4	(3) 34.5	(3) 48.9	(3) 107.6
3135	1700	223	4-5	223	(6) 4.8	(6) 6.8	(3) 7.8	(3) 17.1	(3) 74.8
3240	1675	293	6-7	293	(6) 4.1	(6) 6.4	(3) 11.2	(3) 10.6	(3) 35.3
6145	1650	286	7-8	286	(6) 5.7	(6) 9.1	(3) 16.3	(3) 19.2	(3) 49.3
1045	1650	174	1-8 Duplex	174	(6) 3.8	(5) 4.6	(6) 5.4	(3) 8.5	....

* Analysis = C 0.15%; Mn 1.00%; Si 0.22%; Mo 0.47%.
† Figures in parentheses indicate number of breaks used to compute average.

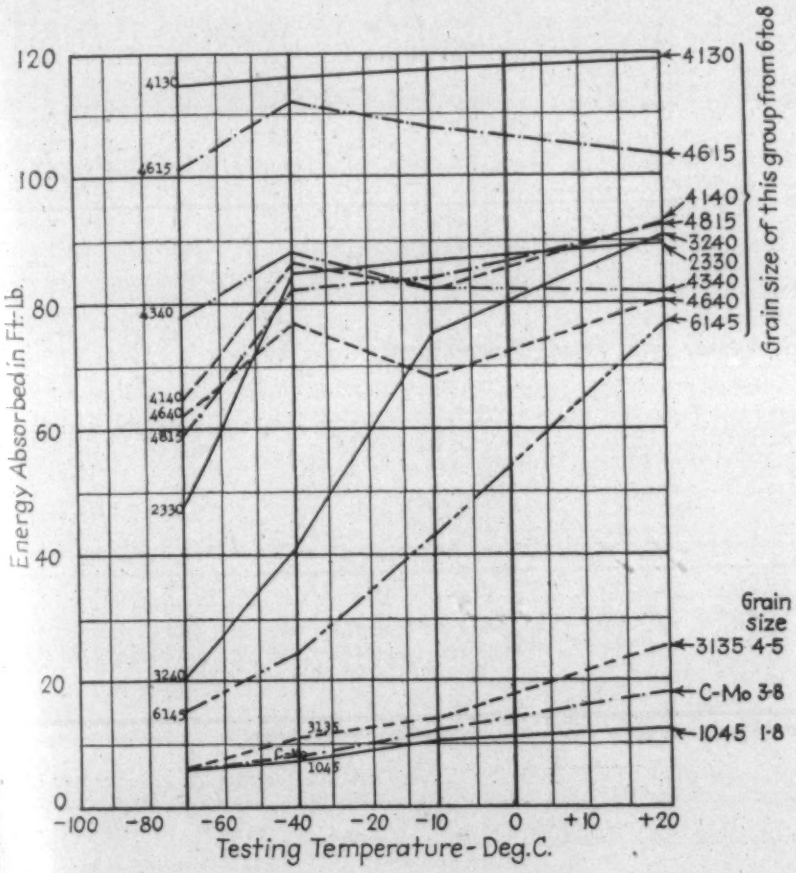

Fig. 3. Average Impact Properties of SAE Steels at Indicated Temperatures.

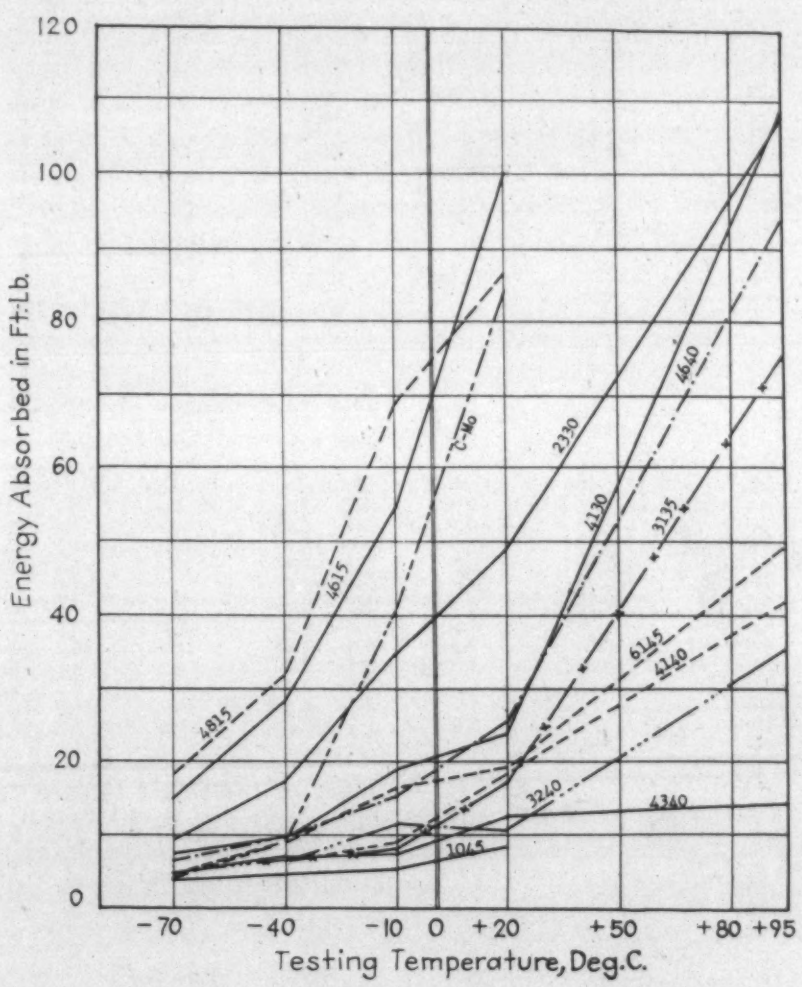

Fig. 3. Average Impact Properties of SAE Steels Indicated Temperatures.

from the cooling bath (with tongs cooled to the same temperature) and the time the blow was struck. It is believed that a negligible temperature rise occurred in this short interval.

Each steel was tested in three different heat treatments, viz:

(1) Normalized at a temperature best suited to the particular analysis (Table 1 and Fig. 1).

(2) Quenched and drawn to a hardness of approximately 200 Brinell (Table 2 and Fig. 2).

(3) Quenched and drawn to a hardness of approximately 300 Brinell (Table 3 and Fig. 3).

Table 2.—Average Impact Properties of Several SAE Steels Drawn to Approximately 200 BHN

Heat Treatment and Hardness						Energy Absorbed in Ft. Lbs. at Indicated Temperatures						
SAE No.	Quenching Temp., Deg. F.	Quenchant	Rockwell "C" After Quench	Drawing Temp., Deg. F.	BHN After Draw	—190° C. or —310° F.	—90° C. or —130° F.	—70° C. or —94° F.	—55° C. or —67° F.	—40° C. or —40° F.	—10° C. or +14° F.	+20° C. or +68° F.
4130	1575	Water	48.5	1260	207	(6) 6.4	(2) 116.9	(6) 119.8	....	(6) 119.8	....	(3) 119.8
4140	1575	Oil	42.5	1240	228	....	....	(6) 72.0	(3) 112.7	(6) 106.9	(3) 117.2	(3) 111.2
4615	1525	Water	42.5	1100	235	(6) 8.1	(3) 119.8	(6) 119.9	....	(6) 119.8	....	(3) 119.9
4640	1525	Oil	44.5	1240	217	(6) 10.7	(3) 71.3	(6) 78.1	....	(6) 105.7	....	(3) 109.9
4815	1475	Oil	37.5	1100	228	(6) 25.3	(3) 117.9	(5) 119.8	....	(6) 119.8	....	(3) 119.8
4340	1525	Oil	45.0	1260	228	....	....	(5) 38.5	....	(6) 73.8	(3) 75.5	(3) 93.5
C-Mo*	1625	Water	36.0	1100	228	....	....	(5) 55.4	....	(6) 77.0	(6) 102.8	(6) 71.0
2330	1450	Oil	40.0	1050	217	(5) 10.4	(3) 95.9	(6) 108.9	....	(6) 104.9	....	(3) 106.2
3135	1500	Oil	45.0	1200	217	....	....	(5) 31.5	(3) 105.2	(6) 109.2	(3) 118.2	(3) 113.8
3240	1475	Oil	44.5	1240	223	(6) 7.8	(3) 81.5	(5) 103.9	....	(6) 113.8	....	(3) 114.4
6145	1525	Oil	44.5	1250	228	....	....	(6) 38.5	(3) 106.2	(6) 101.0	....	(3) 102.6
1045	1525	Water	40.0	940	228	....	....	(6) 7.6	....	(6) 11.4	(3) 33.5	(3) 38.2

* Analysis—C 0.15%; Mn 1.00%; Si 0.22%; Mo 0.47%.
Figures in parentheses indicate number of breaks used to compute average.

The heat treatments with resultant hardnesses of the steels are given in each table. The McQuaid-Ehn grain size of each steel is listed in Table 1.

The Data

It is generally conceded that the impact test is one of the most difficult of the physical tests to perform on metals and obtain reproducible results. It was believed, therefore, that at least three breaks would be necessary to establish a reliable impact value for each test condition. With one exception, the average of at least three breaks was used to determine the values shown in Tables 1, 2 and 3. Where it appeared that the reliability of the data would be improved by making additional breaks, this was done. In several of the tests, particularly at the lowest temperatures, as many as six fractures were made and the results averaged.

Table 3.—Average Impact Properties of Several SAE Steels Drawn to Approximately 300 BHN

Heat Treatment and Hardness							Energy Absorbed in Ft. Lbs. at Indicated Temperatures			
SAE No.	Quenching Temp., Deg. F.	Quenchant	Rockwell "C" After Quench	Drawing Temp., Deg. F.	Rockwell "C" After Draw	BHN	—70° C. or —94° F.	—40° C. or —40° F.	—10° C. or +14° F.	+20° C. or +68° F.
4130	1575	Water	48.5	1075	27	269	(4) 114.9	(4) 116.9	(4) 117.7	(4) 118.7
4140	1575	Oil	42.5	1075	28.4	286	(4) 65.2	(4) 86.9	(4) 82.1	(4) 93.3
4615	1525	Water	42.5	940	30.5	294	(4) 101.3	(4) 112.3	(4) 108.3	(4) 103.4
4640	1525	Oil	44.5	1040	29.6	302	(4) 61.4	(4) 77.4	(4) 69.3	(4) 80.5
4815	1475	Oil	37.5	800	27.3	302	(4) 59.5	(6) 83.1	(6) 83.9	(4) 93.1
4340	1525	Oil	45.0	1100	29.2	302	(6) 77.9	(6) 88.3	(4) 82.2	(4) 81.5
C-Mo*	1625	Water	36.0	650	27.4	309	(4) 5.9	(4) 7.9	(4) 11.8	(4) 18.4
2330	1450	Oil	40.0	875	28.7	286	(4) 47.7	(6) 85.5	(6) 87.2	(4) 89.9
3135	1500	Oil	45.0	875	31.0	318	(4) 6.1	(4) 10.9	(4) 14.4	(4) 26.2
3240	1475	Oil	44.5	1000	27.3	286	(4) 20.3	(4) 40.9	(4) 75.2	(4) 90.8
6145	1525	Oil	44.5	1125	27.7	286	(4) 15.0	(4) 24.0	(4) 43.0	(4) 76.9
1045	1525	Water	40.0	475	30.0	294	(4) 5.9	(4) 7.0	(4) 10.4	(4) 12.6

* Analysis—C 0.15%; Mn 1.00%; Si 0.22%; Mo 0.47%.
Figures in parentheses indicate number of breaks used to compute average.

Table 4a.—Ranges of Individual Impact Tests, SAE Steels Normalized

	—70° C. (—94° F.)		—40° C. (—40° F.)		—10° C. (+14° F.)		+20° C. (+68° F.)		+95° C. (+203° F.)	
SAE No.	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
4130	7.4	5.7- 9.0	9.5	6.2- 15.2	18.9	14.4- 25.9	23.5	21.6- 25.3	108.4	100.7-115.7
4140	4.9	3.7- 6.5	6.1	3.8- 8.7	9.0	7.2- 11.8	18.4	17.6- 20.0	41.7	36.6- 46.4
4615	14.9	13.6- 17.4	28.3	24.7- 32.0	54.2	43.0- 72.8	100.1	99.7-100.4	....	.....
4640	6.5	4.6- 8.1	9.6	5.7- 11.1	15.3	13.4- 17.2	25.5	22.6- 27.9	93.8	88.5-101.5
4815	18.2	16.8- 22.6	31.4	28.5- 38.2	68.6	48.8- 83.3	86.4	73.1- 95.2	....	.....
4340	4.8	3.5- 5.8	6.6	4.9- 10.2	7.5	5.1- 9.7	12.4	9.6- 16.7	14.3	13.0- 15.9
C-Mo	4.8	4.2- 5.3	8.8	7.5- 10.2	40.5	22.2- 54.1	84.3	78.3- 89.4	....	.....
2330	9.3	6.5- 12.2	17.4	16.3- 20.0	34.5	29.6- 39.6	48.9	41.3- 57.7	107.6	104.5-110.9
3135	4.8	3.3- 6.8	6.8	4.3- 8.1	7.8	5.9- 9.5	17.1	14.4- 19.0	74.8	73.1- 78.1
3240	4.1	3.5- 4.8	6.4	5.2- 8.9	11.2	9.1- 14.5	10.6	9.4- 12.0	35.3	33.2- 39.0
6145	5.7	3.5- 6.5	9.1	6.0- 12.3	16.3	15.9- 16.7	19.2	16.4- 21.2	49.3	37.4- 58.7
1045	3.8	3.4- 4.8	4.6	3.4- 5.7	5.4	5.1- 5.7	8.5	6.9- 10.4	....	.....

Table 4b.—Ranges of Individual Impact Tests, SAE Steels Drawn to Approximately 200 BHN

	—190°C.(—310°F.)		—90° C. (—130° F.)		—70° C. (—94° F.)		—55° C. (—67° F.)	
SAE No.	Average	Range	Average	Range	Average	Range	Average	Range
4130	6.4	5.7- 8.7	116.9	114.0-119.8	119.8	(all at capacity)	....	.....
4140	....	.....	....	.....	72.0	62.6- 83.1	112.7	109.6-114.4
4615	8.1	5.7- 11.4	119.8	(all at capacity of machine)	119.9	(all at capacity)	....	.....
4640	10.7	7.8- 16.7	71.3	52.7- 84.0	78.1	52.7-109.7	....	.....
4815	25.3	18.8- 36.5	117.9	115.9-119.8	119.8	(all at capacity)	....	.....
4340	....	.....	....	.....	38.5	25.4- 47.4	....	.....
C-Mo	....	.....	....	.....	55.4	45.3- 76.2	....	.....
2330	10.4	8.8- 11.4	95.9	86.9-108.7	108.9	103.6-115.2	....	.....
3135	....	.....	....	.....	31.5	24.4- 42.1	105.2	95.4-112.1
3240	7.8	5.9- 9.1	81.5	63.5-105.5	103.9	96.7-113.3	....	.....
6145	....	.....	....	.....	38.5	34.5- 48.9	106.2	104.8-108.2
1045	....	.....	....	.....	7.6	4.6- 10.1	....	.....

	—40° C. (—40° F.)		—10° C. (+14° F.)		+20° C. (+68° F.)	
SAE No.	Average	Range	Average	Range	Average	Range
4130	119.8	(all at capacity)	....	.....	119.8	(all at capacity)
4140	106.9	96.2-112.2	117.2	114.7-119.8	111.2	104.5-115.3
4615	119.8	(all at capacity)	....	.....	119.9	(all at capacity)
4640	105.7	100.1-110.6	....	.....	109.9	108.2-111.9
4815	199.8	(all at capacity)	....	.....	119.8	(all at capacity)
4340	73.8	25.4-101.9	75.5	54.9-108.2	93.5	90.3- 98.9
C-Mo	77.0	51.7- 95.0	102.8	89.6-111.7	71.0	59.5- 87.4
2330	104.9	98.3-112.2	....	.....	106.2	105.7-106.5
3135	109.2	98.9-115.1	118.2	114.9-119.8	113.8	110.2-116.7
3240	113.8	104.2-119.8	....	.....	114.4	113.0-115.4
6145	101.0	91.4-110.0	....	.....	102.6	95.8-109.6
1045	11.4	8.1- 17.4	33.5	27.2- 41.7	38.2	18.3- 50.9

Table 4c—Ranges of Individual Impact Tests, SAE Steels Drawn to Approximately 300 BHN

	—70° C. (—94° F.)		—40° C. (—40° F.)		—10° C. (+14° F.)		+20° C. (+68° F.)	
SAE No.	Average	Range	Average	Range	Average	Range	Average	Range
4130	114.9	113.1-117.3	116.9	111.5-119.8	117.7	113.8-119.8	118.7	115.3-119.8
4140	65.2	46.0- 71.9	86.9	80.5- 91.8	82.1	79.8- 83.4	93.3	87.8- 99.7
4615	101.3	93.8-114.3	112.3	110.0-117.8	108.3	99.5-112.5	103.4	93.3-109.5
4640	61.4	55.9- 67.8	77.4	74.0- 80.8	69.3	65.0- 73.7	80.5	73.8- 85.8
4815	59.5	44.6- 66.7	83.1	76.2- 90.5	83.9	77.3- 90.7	93.1	83.3-107.2
4340	77.9	72.1- 83.6	88.3	74.1-105.2	82.2	75.2- 94.0	81.5	73.3- 92.7
C-Mo	5.9	4.7- 7.8	7.9	7.3- 8.4	11.8	10.7- 13.3	18.4	13.7- 24.0
2330	47.7	38.0- 66.9	85.5	63.0-108.5	87.2	77.5-102.7	89.9	84.3- 95.4
3135	6.1	4.9- 7.0	10.9	8.5- 12.9	14.4	11.4- 15.9	26.2	23.5- 27.2
3240	20.3	17.4- 21.7	40.9	35.0- 47.6	75.2	71.7- 77.3	90.8	69.4-109.4
6145	15.0	13.2- 16.8	24.0	20.7- 26.1	43.0	31.6- 65.7	76.9	71.0- 89.8
1045	5.9	4.8- 6.8	7.0	5.7- 9.3	10.4	8.1- 13.3	12.6	7.6- 22.8

For the benefit of those who may wish to look beyond the average results to the extreme values obtained for individual tests at specific temperatures, the ranges are given in Table 4 (a, b, c). The number of tests made to establish these ranges is shown in Tables 1, 2 and 3. The most notable case of variation was 4340, 200 Brinell, at −40 deg. (Table 4b).

Because SAE steels numbered 4130, 4615, 4640, 4815, 2330 and 3240 were found to be very tough when quenched and drawn to 200 Brinell and cooled to −70 deg. C., these steels were also tested at −90 deg. C. and at −190 deg. C.

Discussion of Results

Comparison of the results shown in Table 1 with Tables 2 and 3 emphasizes the importance of heat treatment to improve the sub-zero impact strength of steel. There is also evidence to show that the alloy steels are superior to a plain carbon steel in the matter of low temperature impact strength.

Because the steels selected for study necessarily vary in carbon content, it is quite impossible to measure quantitatively the effect of individual alloys on sub-zero impact properties. Such an evaluation would justly be the subject of a separate investigation. It can be said, however, that in the case of molybdenum, this element appears more effective in improving impact strength of steel at low temperatures when used in conjunction with nickel or chromium, or both. This is especially true when comparing the sub-zero properties in the normalized condition.

It should be pointed out that the low energy values reported for the carbon-molybdenum steel ought to be considered as being somewhat lower than normal expectancy since this steel was found to have a duplexed grain size, indicating improper deoxidation or rolling. In other work it has been found that incomplete deoxidation tends to reduce the impact strength at low temperature. It is apparently advisable to use the carbon-molybdenum steel in the fine grained state to obtain satisfactory resistance to shock at low temperatures.

In conclusion, it may be said that of the 12 steels studied, only 4615 and 4815 have satisfactory low temperature impact strength (i. e., in excess of 10 ft. lbs. at −70 deg. C.) when in the normalized condition (Fig. 1) In the quenched and drawn to 200 Brinell condition, all steels except 1045 have satisfactory low temperature impact strength (Fig. 2). In the quenched and drawn to 300 Brinell condition, all steels except C-Mo, 3135 and 1045 have satisfactory sub-zero impact properties (Fig. 3).

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Heterogeneity of Steel Ingots--*(Continued from page 89)*

The authors noted (1) that the increase in FeO in the slag (see Fig. 1) corresponds with the increase of FeO, MnO, and SiO_2 in the steel and with the decrease or oxidation of the Mn, Si and C in the metal; (2) the FeO falls rapidly with the recarburizing of the bath in the refining period; (3) throughout the heat the C in the metal was inversely proportional to the FeO content of the metal.

Gases and Ingot Solidification

The effect of passing argon through liquid steel was studied by Swinden and Stevenson[4] as an amplification of a previous report that had indicated a fundamental difference between the effects of hydrogen and of nitrogen when passed through molten steel. Hydrogen had been observed to cause pronounced unsoundness, whereas nitrogen caused no unsoundness and in addition was capable of preventing hydrogen unsoundness if passed through the steel following treatment of the latter with hydrogen. The authors had interpreted this as corroboration of the belief that hydrogen is much more soluble in liquid than in solid steel, whereas nitrogen is not. Others, however, had suggested that the nitrogen failed to cause unsoundness because of the formation of iron nitride, and that this chemical basis for explaining the soundness of nitrogen-treated steel be checked by using an inert gas like argon.

The authors did this, and found that argon behaves exactly as did nitrogen. Because the argon cannot form a compound with the iron and the nitrogen can, they conclude that the difference between the effect of nitrogen and hydrogen on liquid steel cannot be explained on the basis of chemical reaction between the gas and the iron.

Experiments using moist air and moist argon showed that moisture tends to cause unsoundness under circumstances in which the passage of dry gas caused none.

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A NOTE ON

Beryllium-Aluminum Alloys

FOR AIRCRAFT PISTONS

by J. B. Johnson

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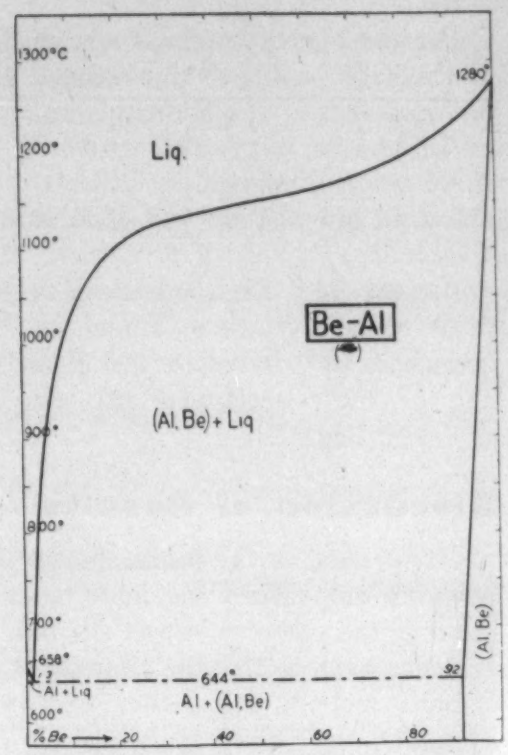
THE BERYLLIUM-ALUMINUM ALLOYS have been suggested for the manufacture of pistons for aircraft engines. The results of tests of sand cast test bars are of interest due to the scarcity of data for these alloys. The tensile properties were determined at room temperature and 500 deg. F. The low strength at room temperature may be due to the low ductility.

The chemical composition of the alloy was:

	Per Cent
Beryllium	67.43
Silicon	0.34
Copper	0.12
Iron	0.69
Manganese	0.90
Chromium	0.06
Aluminum (by difference)	30.46

The mechanical properties of the alloys at room temperature and at 500 deg. F. are as follows:



The Beryllium-Aluminum Equilibrium Diagram (Oesterheld)

	Room	500° F.
Tensile strength, lbs. per sq. in.	13,700	10,480
Yield strength (0.001 in. per in.) lbs. per sq. in.	13,600	—
Proportional limit, lbs. per sq. in.	3,700	—
Elongation, in 2 in. per cent	0	1
Modulus of elasticity, lbs. per sq. in.	20,400,000	—
Brinell hardness	75	57[1]
Thermal conductivity, cal. per sq. cm./cm./sec./deg. C.	—	0.22
Specific gravity	2.05	—

[1] After cooling.

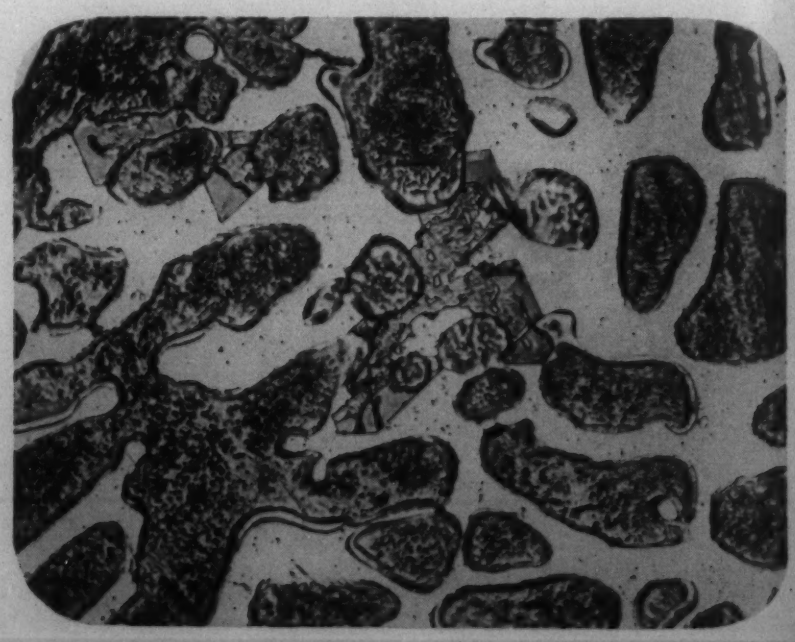
The modulus of elasticity was obtained with two diametrically opposed Tuckerman strain gages.

The tensile strength at 500 deg. F. and Brinell hardness after heating are approximately equal to similar properties for the forged 14 per cent silicon-aluminum alloy extensively used for aircraft pistons. The conductivity is approximately one-half, which would cause the beryllium-aluminum pistons to operate at a higher temperature, which is a less favorable condition.

The micro-structure revealed by the accompanying photomicrographs, is a network of hard eutectic and softer matrix.

Average Structure of Be-Al Alloy. 100 X. Unetched.

Average Structure of Be-Al Alloy. 500 X. Etched with Dix reagent (HNO_3 2.5 c.c., HCl 1.5 c.c., HF 1.0 c.c., H_2O 95.0 c.c.)



PROTECTING METAL SURFACES WITH

Modern Lacquers and Enamels

by G. Klinkenstein

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NON-METALLIC FINISHES ARE APPLIED to metal products for two purposes: To make the products attractive in appearance, and to protect them from corrosion.

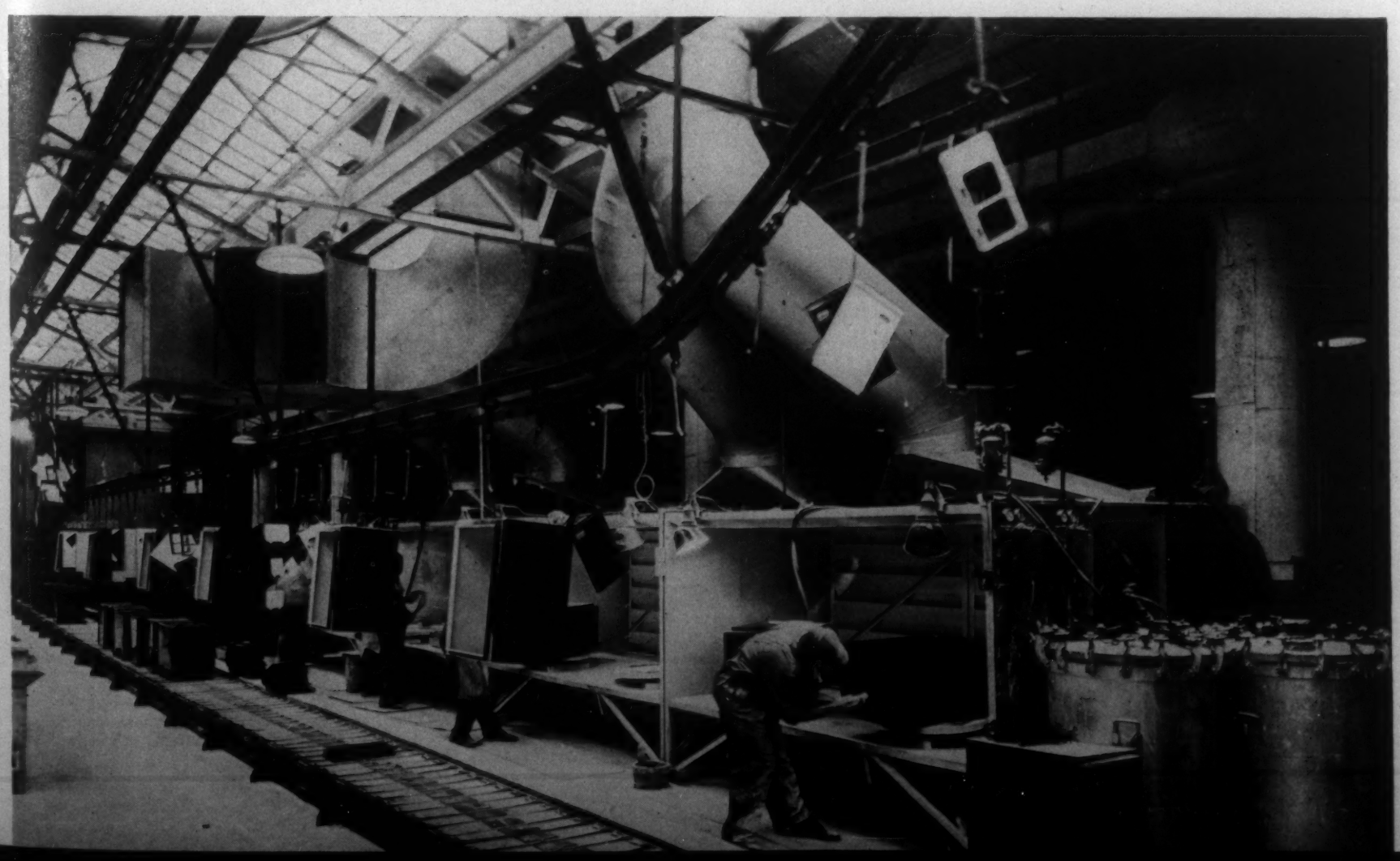
In meeting the first of these requirements, the finishing industry has been extraordinarily successful. Virtually every color, texture, degree of gloss, and lustre known to man can be reproduced with modern finishes, and new decorative effects are being constantly devised.

As to protection, the ultimate goal—i.e., permanent protection—is unattainable, but relative progress in this direction is continuous. Every research laboratory in the finishing industry is engaged in developing finishes that will provide more lasting protection for metals under various conditions, and every year sees finishes produced that definitely lengthen the useful life of certain metal products. The economic importance of this work can hardly be exaggerated. The annual loss due to the corrosion of metals is enormous, and to reduce this loss by even a small fraction means large savings to society at large.

Protective Coatings for Non-Ferrous Metals

Of the several different kinds of non-metallic finishes (paint, varnish, enamel, japan, and lacquer), the one that is chiefly used for finishing products made of non-ferrous metals is lacquer.

Finishing Refrigerator Cabinets. Refrigerators must look well and retain their good appearance under the most severe service conditions. Hence, the durability of their finish is all important. (Courtesy: The DeVilbiss Co.)



Lacquer is a solution of nitrocellulose, or pyroxylin, and other substances in suitable solvents. After it is applied, the solvents evaporate and leave behind a film resembling celluloid, which "air-dries out of dust" in a few minutes at ordinary temperatures (and even more rapidly when "force-dried" at temperatures around 100 deg. F.), and becomes permanently hard in a few hours. Unlike enamel, lacquer does not have to be baked at relatively high temperatures to hasten hardening and increase its durability. Its rapidity of drying, together with the durability of its film, makes lacquer especially suitable for finishing products turned out in quantities. Lacquer is supplied in both clear and pigmented forms. Clear lacquers are used for protecting natural metallic surfaces; with pigmented lacquers (called lacquer-enamels), any desired color effect can be secured.

A film of pure pyroxylin or nitrocellulose is hard, nonporous, resistant to moisture and acids, and chemically inert towards metals. Hence, it forms an excellent basis for a protective coating for metals. Pyroxylin alone, however, cannot be used for lacquer manufacture. In order to produce lacquers that are tough and flexible, that adhere well to metal surfaces, and have good flowing and drying characteristics and other necessary properties, certain substances, which are called "plasticisers," and gums, resins, vegetable oils, and certain organic compounds, have to be added to the pyroxylin base. In consequence, the composition of lacquers is fairly complex, and their physical and chemical properties vary with the constituents used in their manufacture.

Because of this variability, there may be wide differences in the protective powers of different lacquers, even though they look exactly alike. A given lacquer may be well suited for use on one metal, but not on another—its film may react with the second metal, or with its corrosion products, and quickly disintegrate.

This circumstance has compelled lacquer manufacturers to study carefully the requirements of each metal in order to develop lacquers that will provide maximum protection for each one. In general, a lacquer intended for one metal should not be used for another—even copper and brass, for best results, require lacquers of different composition.

Lacquers for Al, Zn, Mg and Cd

The finishing requirements of copper, brass, bronze, silver, and nickel are thoroughly known, and excellent lacquers for each of these metals can be obtained without difficulty. Care should, however, be taken in selecting lacquers for aluminum, zinc, magnesium, and cadmium. The corrosion products of these latter metals combine actively with many of the commonly used lacquer bases, and, until recently, it was thought impossible to produce lacquers that would adhere well to these metals and protect them for any length of time. These difficulties have been overcome, however, and special lacquers, both clear and pigmented, can now be obtained for finishing these metals. This advance has greatly extended the possibilities of using aluminum and zinc in their natural finishes. It should be mentioned, however, that no clear lacquer for these metals that will adequately protect them in out-of-doors service has as yet been developed.

Die castings made of alloys of aluminum, zinc, and magnesium can be finished with suitable lacquers just as they come from the mold, provided they are clean and are not coated with oxides, or scale. In the latter case, the castings must be treated, before finishing, so as to prevent progressive oxidation and insure adherence of the lacquer film. Several different solutions have been developed for this purpose. One causes the deposition of a coating of phosphate on the surface of the metal, and another the deposition of another kind of metal in finely divided form. Such pre-treatment is advisable in any case if the product is to be used out-of-doors.

Among recent developments are finishes for zinc die castings that exactly reproduce naturally finished copper, brass, and bronze. The use of these finishes makes possible the substitution of zinc for the more expensive metals in the manufacture of many products.

Chromium, being immune to the action of the atmosphere, needs no lacquer for its protection. If, however, it is desired to color or enamel chromium, trouble may be encountered, because no known air-drying lacquer will adhere well to a polished chromium surface. To overcome this difficulty, a special clear chromium primer is applied to the parts which are to be colored, and is then baked. This coating adheres strongly to the metal and furnishes an excellent foundation for any desired kind of lacquer-enamel.

Finishes for Severe Service Conditions

Service conditions must also be taken into consideration in determining what kind of a finish is to be used on a given product. Some products are carefully protected by their owners and are rarely handled, while others are subjected to the roughest kind of treatment and exposed to the action of all sorts of destructive agencies. As the life of many products is measured by the life of their protective coatings, it is often of the utmost importance to select finishes that will best suit the service requirements.

Among the destructive factors, which most frequently have to be taken into consideration, are the following, in various combinations:

Abrasion, as on table tops.
Constant rubbing, as on hand rails.
Bending and folding.
Exposure to the weather.
Sunlight.
Moisture.
Salt water.
Weak acids, such as fruit juices and vinegar.
Weak alkalies, such as ammonia water and soap suds.
Greases and oils.
Alcoholic drinks.
Perspiration, as on flashlights, handles, and rails.
Saliva, as on toys.
Heat.
Match flames and glowing cigarettes.

The lacquer film is tough and durable, and as its physical and chemical properties can be varied at will over a wide range by the lacquer chemist, many of these service requirements can be satisfactorily met with lacquers and lacquer-enamels. But another group of finishes—the synthetics—are even more durable, and their use is constantly increasing for products where the maximum of protection is desired.

Synthetic Finishes

Synthetic finishes are a comparatively recent development. Their special characteristic is that they contain syn-

Finishing Lawn Mowers. Rapidity of production counts in this type of work, and "speed-up" finishes in brilliant, attractive colors are indicated. (Courtesy: The DeVilbiss Co.)

thetic resin bases, which are allied to the plastic molding compounds. When these finishes are applied to a product, they air-dry hard like the lacquers (though more slowly), but when the finished product is baked at temperatures of 200 deg. F., or higher, the synthetic resins "polymerize" and become insoluble and infusible. Some of the resins used in these finishes (e.g., the phenol-formaldehyde group) are very resistant to acids and alkalies; others (e.g., the alkyds) stand exposure to the weather and the ultraviolet light of the sun; and others have still other desirable properties. By properly selecting and combining these bases, clear or pigmented finishes of remarkable durability for various services can be obtained.

The durability of finishes is determined in advance of their use by means of "accelerated" tests devised to simulate any given combination of service conditions. Such tests give information of great value, but they cannot wholly take the place of the performance records of a finish under actual service conditions.

Heat-Resisting Finishes

Heat is a service condition of special importance in the selection of industrial finishes. Ordinary lacquers, enamels, and varnishes cannot be used on products frequently exposed to temperatures above 200 deg. F., since, in time, they will lose color, become brittle, and peel off. There is, however, a special group of heat-resisting finishes that can be used on electric light fixtures, heaters, and other products that are normally subjected to elevated temperatures. This group consists of the following:

Finish	*Color*	*Max. Safe Temp. Deg. F.*
Air-drying heat-resisting lacquers	Clear, all colors	250 to 300
Baked synthetic enamels	Clear, all colors	300 to 350
Baking Japans	Black	400 to 450
Aluminum paints	Natural metal	400 to 1000
Burn-proof lacquer	Clear golden	Match flame

Lacquers for "Oxidized" Metals

Special lacquers are required to protect products of copper, silver, or nickel with "oxidized" finishes; that is, with surfaces darkened by treating them with sulphide solutions.

When a metallic sulphide coating is thus formed and it is afterwards covered with ordinary lacquer, it is liable to a defect known as "crystal spotting." Crystal spots are small, dark aggregates of metallic sulphide which appear under the lacquer coating. Research has shown that such crystals are formed when the "oxidized" surface comes into contact with sulphur, either as hydrogen sulphide in the air, or free sulphur in paper, rubber bands, and other packing material. The lacquer appears to play no part in the process except to hold the crystals in place, when formed.

As long as "oxidized" products remain under the manufacturer's control, crystal spotting can be avoided by protecting the products from coal gas and other sources of hydrogen sulphide, and by packing them carefully in sul-

Finishing Gas Meters. Protection for the largest possible time rather than good looks is the principal requirement for a finish for products of this kind. (Courtesy: The DeVilbiss Co.)

phur-free wrappings. But as neither dealer nor user can be expected to take similar precautions, further protection of some sort is necessary. This is provided by finishing the products with special lacquers which are fairly impervious to sulphur. These lacquers do not constitute infallible safeguards, but they do greatly reduce the number of rejects due to this cause.

Lacquers for Plated Ware

When clear lacquers are used for finished electroplated products, special precautions have to be taken to avoid the defect known as "stain-spotting." Stain-spotting is caused by the presence of traces of salts from the plating bath (especially the cyanides) in the pores of the deposited coating or the base metal. It is almost impossible to remove the salts completely by rinsing, no matter how often repeated, yet if any particles remain in the product, they tend to absorb moisture and form solutions, which spread over the surface and form unsightly spots and stains.

This tendency to stain-spotting is minimized by carefully controlling every step of the cleaning and plating process and by finally finishing the products with special lacquers. In one procedure, the final steps are to bake the products, in order to dehydrate the residual salts and render them inactive, and, immediately on cooling, to finish them with a special "non-stain-spot" lacquer, which gives a fine, durable finish suitable for either indoor or outdoor use.

In another procedure, the products are not baked. In this case, as soon as they come out of the last rinsing bath, they are dipped into what is known as "water-dip" lacquer, a special solution of gums, which has the property of adhering to a wet metal surface. This finish seals up the pores of the product and renders the included salts harmless. It can be used as a final finish, if the appearance of the product is of little importance, or it can be used as the foundation for a finer finish.

When pigmented lacquers are used, no special precautions against stain-spotting need be taken, as the stains do not show through the opaque coating.

Protective Coatings for Ferrous Metals

The lacquers and enamels used for finishing non-ferrous metals are also widely used for finishing iron and steel products. They cannot be used alone, however. Though they are capable of protecting the surface they cover from air and moisture, corrosion, starting at any unprotected point, will creep under the finish and ultimately destroy it. They must be applied over a suitable foundation.

For sheet steel products, the most durable foundation consists of a coat of synthetic primer baked on rust-proofed

metal. The number and character of the upper coats will depend upon the product and its service. For high-grade automobiles, where the maximum of beauty and protection is desired, upward of 14 coats of lacquer may be applied. For electric refrigerators, which are subjected to very severe service conditions, two coats of baked synthetic enamel over the synthetic primer are generally used. For air-conditioning units, one finishing coat of baked synthetic enamel has been found to suffice. For products in still less severe service, the finishing coat can consist of any kind of lacquer-enamel.

For iron castings, special air-drying primers have been developed as under-coats for lacquer finishes. These primers adhere strongly to the metal, fill up file marks and other irregularities, sand easily, and form a firm bond with the lacquer finishing coats. A widely used undercoat for oil burners, domestic stokers, and other products that must withstand marring, moisture, etc., consists of a crackle finish, which can be baked directly on the rough metal and afterwards finished with lacquer enamel.

For protecting iron and steel surfaces that are exposed to corrosion, but can not conveniently be rust-proofed, such as steel for construction, railroads, and shipbuilding, special anti-corrosive finishes have been developed. These finishes contain rust inhibitors and offer a high degree of protection against the effects of moisture, salt water, weak chemicals of various kinds, and electrolytic action.

Finishes to Suit Manufacturing Processes

Besides being properly adapted to the product and the service, an industrial finish must also be suited to the process by which the product is being manufactured. Two finishes may be equally good, as finishes, but one may cost much more to apply under given conditions and with given equipment. The finishing department should never be a "bottle-neck." If it is, there is something wrong with the tempo of the process and finishes should be found that will speed it up.

Some finishes will not adhere well to metal surfaces unless they are perfectly clean; but sometimes it is an expensive matter to clean products perfectly before finishing, and, in such cases, it is often possible to use finishes that are tolerant towards a little grease, dirt, or buffing compound.

In many shops, the use of a finish that dries out-of-dust more rapidly than the one being employed will cut down the number of rejections due to dust spots on the finish; and, similarly, if the percentage of products that have to be touched up before shipment is high, this may often be remedied by using a different finish.

It is often economical to stamp or form products out of pre-finished raw materials or to finish a product before it is machined or engraved. Special finishes can be obtained that are suitable for this kind of work.

The present tendency in industrial finishing is to cut down as much as possible the time required for finishing in order to speed up production, reduce costs, and lower inventories. This can often be done, without sacrificing the quality of the finish, by the use of some of the newer developments in the finishing field which have been developed specifically for this purpose.

Industrial Finishing Has Become A Science

From what has been said, it is evident that the number of highly specialized industrial finishes has become very large. Industrial finishing has, in fact, ceased to be only an art; it has also developed into a branch of engineering science. The "rule-of-thumb" era has passed away in the finishing field, and the properties of finishes must be studied from an engineering standpoint, just as the properties of other raw materials are being studied, before they can be utilized effectively and economically.

It would be easier, for both the production engineer and the manufacturer of finishes if the number of finishes could be reduced and a few of them standardized, but in the present state of the art this is impracticable; the tendency, in fact, is in the other direction. Nor can one quarrel with this state of affairs, since, because of it, metals are being given better protection, production costs are being reduced, and the markets for the finished products have been greatly widened.

A CORRELATED ABSTRACT ON

The Use of Electron Diffraction

IN STUDYING CORROSION

Part II

(Concluded from the March Issue)

by I. R. Landau

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Passivity and Inhibitors

A special case of films on massive metal surfaces is passivity. There is no significant work by electron diffraction methods that deals specifically with passivity, except that of Thomson[14], who, in most cases, found no oxide patterns on iron kept passive throughout the experiment; in general his results were negative, and did little to clear up the disputes concerning the theories of passivity. This, then, offers a fertile field for investigation. There are many phenomena connected with this subject, such as the anomalous behavior of certain alloy steels that are obscure, but which may be elucidated by using this new technique.

Recently, a note by Iitake, Miyake, and Iimori[46] indicated that the apparently *amorphous* film on pure iron passivated in dichromate, gave a γ-Fe_2O3 pattern by *transmission,* when stripped electrolytically. If confirmed, significant results may be expected to follow. In fact, it seems that the whole question of the nature of the bond between the film and the metal has not been solved (attention should be given to the theories of Langmuir[47]). In any event, it seems likely that the highly protective films are "amorphous", and crystalline films, if known to be protective, should be regarded critically. An opinion held by some is that the protective agent lies beneath the crystalline layer, and its nature is bound up with the question of the film-metal bond. A rich field for investigation is possible here, though perhaps a difficult one, at least by electron diffraction methods.

Related somewhat to the subject of passivity is that of inhibitors. There is little information available as to the processes that occur when quinoline, positive colloids, or other inhibitors come in contact with a metallic surface. A fundamental insight into such reactions would be of great theoretical and practical value, but it is doubtful that electron diffraction is the answer to this problem; the adsorbed film is probably too irregular, and a lack of satisfactory crystalline properties would render the method void. Furthermore, if the metal is removed from contact with the inhibitor and subjected to high vacuum, serious changes may take place. This latter objection may be valid in many other corrosion problems as well, and must not be neglected.

In the miscellaneous classification may be grouped studies of special cases, the phenomena of which are especially obscure at present, and for which other methods are valueless or nearly so.

Rust

For example, even the common case of rusting is not too clear, and Nelson[12] correctly points out that despite the importance of the subject, few have studied iron films. Cates[30] examined rust, and observed it to be largely γ-FeOOH. The mineral Rubinglimmer was proved to have the same structure; obviously, by studying the mineral, much can be learned about the properties of the rust, and its formation. This is the procedure that occurs most often: experimental data for the unknown film are observed to be identical with the constants of well known compounds or minerals, and predictions concerning chemical, electrical, and consequently corrosion resistant properties are thus permissible. Further examples of such analogies to minerals are given by Bragg and Darbyshire[31], who report that tin, lead, zinc, nickel and copper, when molten, were covered with SnO_2, PbO_2, ZnO, NiO, and Cu_2O respectively.

Another important paper was that of Smith[20], who investigated the structure of thin metal oxide and hydroxide films. The comparatively thick films removed from heated metals by electrolysis were polycrystalline, and were the normal oxides NiO, Cu_2O, and Fe_3O_4, on the respective metals. He found no preferred orientation, however, and noted that in the case of iron, heating to 1110 deg. F. gave patterns strongly resembling those of the γ-Fe_2O_3 used as a

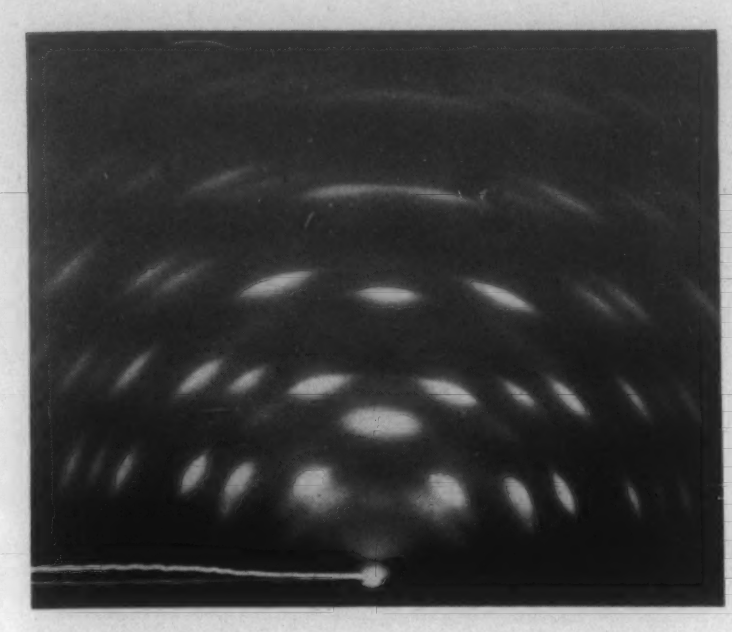


Fig. 8. Iron Mirror Exposed to Air for 2 Minutes.

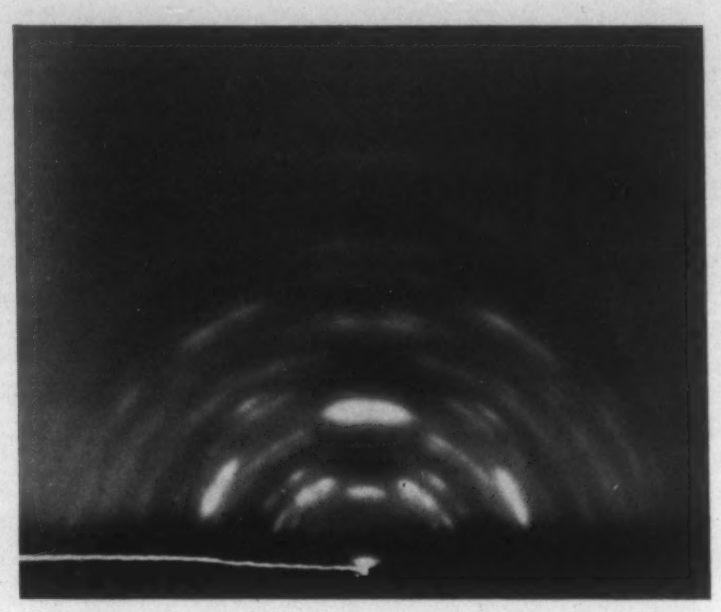


Fig. 9. Same Surface After Heating in Air at 200 Deg. C. for 15 Minutes.

When mirrors are formed by vaporizing iron onto flat surfaces in a vacuum, each iron crystal is oriented with a (111) plane parallel to the surface, and the resulting diffraction pattern consists of short arcs which lie on equally spaced lines parallel to the surface of the sample. Thus, in Fig. 8 the pattern from such a surface shows equally spaced horizontal rows of spots which are due to iron. Those spots which do not fall on the parallel lines are due to an invisible film of oxide formed on exposure of the sample to dry air at room temperature for 2 minutes. After heating the sample in air at 200° C. for 15 minutes, the iron pattern had completely disappeared, leaving only the oxide pattern, Fig. 9, although the surface had not undergone any visible change. The spot pattern of the air-formed oxide (γ-Fe_2O_3) superimposed on the oriented iron pattern suggests that there is a definite orientation relationship between the oxide crystals and the underlying iron crystals. From measurements on these plates it has been possible to show just what this relationship is. (Courtesy H. R. Nelson, Battelle Memorial Institute.)

standard. Nelson was the first to study the massive metal. He observed patterns structurally identical with Fe_3O_4 (or γ-Fe_2O_3) with the oxide having a definite orientation relative to the underlying iron [Figs. 8 and 9]; the film forms very rapidly when exposed even to low air pressures. He found good agreement between patterns from evaporated iron and those from the massive metal.

Non-Ferrous Oxides and Tarnishes

In another study, Finch and Quarrell[32], examined partially and completely oxidized zinc films; they discovered that a ZnO pseudomorphic with zinc was formed by oxidation. It is soon converted to normal ZnO, but the conversion product remains separated from the metal by a layer of pseudomorphic oxide. According to them, it is this pseudomorphic oxide that confers corrosion resistance on zinc. In the light of more recent work, however, it is now uncertain whether the facts are entirely represented by this paper.

Trillat and Oketani[33] carried out work of a related character; they studied the effect of heating a metal in inert gases, a vacuum, and oxygen. It was their desire also to investigate the appearance of supplementary rings, which Rideal[6] attributed to a solution intermediate between adsorption and a true compound. They tried pure gold first: the metal pattern alone was found up to 1020 deg. F.; then color changes occurred and new patterns appeared. Above 1110 deg. F. these grew stronger and stronger; a fluorescent screen gave a picture of the changes as they occurred. The intermediate pattern between 1020 and 1110 deg. F., they concluded, was due to a superficial fluidity of the atoms, which gradually disappears at higher temperatures, and is replaced by the normal pattern of recrystallized gold. There was no difference of behavior in oxygen. However, gold containing 1.5 per cent silver and 1 per cent copper, which behaves similarly to pure gold in inert gases or a vacuum, gives a new type of diagram in oxygen due to an "interstitial solid solution of O_2 intermediate between the adsorption of Langmuir and true combination." Apparently the presence of oxidizable elements facilitates this oxygen combination. The behavior of silver was similar; but aluminum and copper formed permanent oxides in air. The authors also point out the importance of their studies (including organic compounds on the surface which may give extra rings) in connection with adsorption and catalysis, and recrystallization as a function of temperature.

In a similar vein, Burgers and Amstel[34] investigated layers of metallic barium, obtained by volatilizing the metal in the camera. They found that on oxidation, the oxides formed oriented layers determined largely by the orientation of the metal underneath; consequently they are closely related. That this may be of significance in corrosion is clearly apparent.[19] Nelson[12] and Beeching[25] have observed similar effects. Recently, Quarrell[35] studied thin films of many metals, including cobalt, palladium, etc. prepared by evaporation, electrodeposition, and chemical deposition; he found in numerous cases extra rings and bands, which he shows are typical of the crystal structure rather than of the metal. He discusses the changes that occurred in lattice structure during deposition, etc. Such studies may be of great importance in investigations of protective coatings, etc.

The work described above would be difficult to accomplish by other means, and serves to demonstrate how many common metallic problems were little understood until electron diffraction came into use. With regard to tarnishes, some work[38] has been done by X-rays; liquid metal surfaces were studied by reflection, and the structure of tarnish films disclosed. But as the temperature increased the tarnish films became thinner, and could not be satisfactorily examined. The tarnishes on silver have been studied to determine rates of formation, composition, etc., although not usually by X-rays. Many other metallic objects suffer tar-

nishing when used, or when manufactured. In all these cases, if the tarnish film is very thin, electron diffraction offers a possible method of investigating these phenomena.

The field of metal finishes is also becoming increasingly significant. The treating of finished steel with certain chemicals causes the appearance of colored films of various compositions and thickness. The presence of other elements helps in producing these artificial coatings. Such phenomena, also, may very profitably be examined by electron diffraction.

Non-Integral Protective Coatings

Finally, we may consider a field somewhat related to the preceding, namely protective coatings, platings, painted finishes, etc., which are closely connected with the problem of corrosion. It must be borne in mind that electron diffraction can be used in studying surface conditions, and since protective coatings in general are by no means as thin as the protective oxide films on metals, the method can be used to investigate certain features of these layers inaccessible to other methods.

Adhesion to the base metal is an important property, and is undoubtedly determined by the surface condition of the base metal. Finch and Sun[36] studied the structure of electro-deposited metal surfaces by electron diffraction and found that the structure of the substrate on which the metal is deposited profoundly affects that of the deposit, in that the orientation of the base determines the orientation of the deposit. Similar investigation with other types of coatings may be of value.

The painting of the surface of the protecting layer on any ordinary metal surface is affected by the superficial characteristics. New[32] states very definitely that the "pseudomorphic" zinc oxide would materially influence painting characteristics.

Naturally, the formation of films on the coat is as important as the presence of films on any metal surface. A protective film on a protective coating is doubly effective. Thus zinc coatings, in air, form zinc compounds which add materially to the life of the metal.

The actual composition of the surface layers of a protective coating may be different from the body and it is naturally of great importance to establish its nature. According to Speller[37] the composition of some protective coatings varies with the distance from the base metal. The alloys near the base metal apparently afford little electrolytic protection, so that from this standpoint the outer layers are most important. Consequently, electron diffraction studies of the surface structure may offer some clue as to the appropriate thickness necessary for a desired composition. Also, this surface varies with the process employed (as with zinc), and some additional information may be secured concerning the desirable methods of preparing a coating.

Limitations of Electron Diffraction

THROUGHOUT the discussion of all these applications, it has been apparent that there are certain limitations of electron diffraction which make its utility anything but universal. These, and others which have not been mentioned, may be conveniently summarized as follows:

1. Because the angular deviation of the diffracted beams is small, reflection samples must be smooth, and either flat or convex. Consequently, very rough surfaces, such as are often encountered in severe corrosion cases, can not be treated by this method, and corrosion pits, normally of great interest from a research standpoint, can not be examined by reflection. And, as previously mentioned, reflection in itself offers a much wider field than transmission.

Fig. 10. Heat-Treating Stain on Carbon Steel.

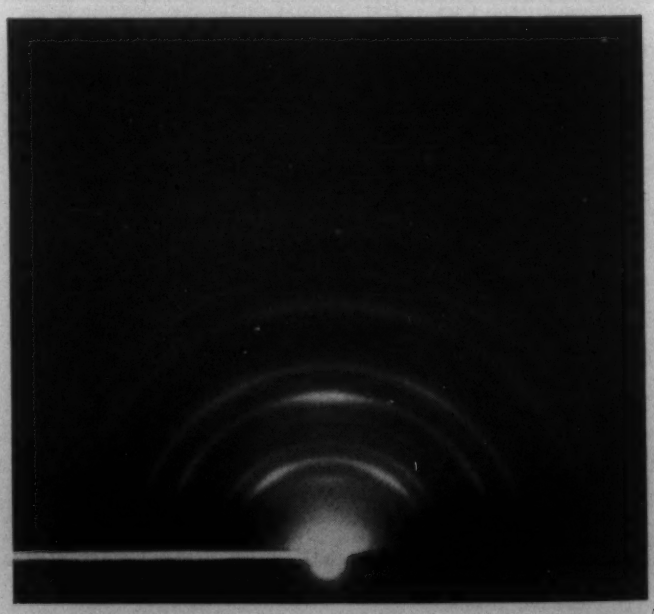
A polished sample of a low-carbon steel acquired a slight stain when heated at 600° F. in the "reducing" atmosphere of partially burned natural gas (6:1 gas-air ratio). The electron pattern proved the stain to be a film of Fe_3O_4. (Courtesy H. R. Nelson, Battelle Memorial Institute.)

2. Refraction at a smooth surface may often cause serious distortions in the patterns. Thomson[39] discusses this and other phenomena connected with the small scale structure of surfaces. He shows that, owing to a difference in potential inside and outside the metal[40], there is a shift in the ray closer to the crystal surface. A wavy surface may even destroy the pattern. The effect is especially noticed in etched surfaces, when the beam enters and leaves by the same face. In general, the pattern tends to become more diffuse, extra rings may occur, or if variable refraction occurs, the pattern may be obliterated entirely.

3. Many surface films that are not crystalline or exten-

Fig. 11. Tarnish Stain on Copper.

A polished piece of copper was immersed in water through which H_2S was bubbled. The sample was then left in pure water for a day. The diffraction pattern proves that the resulting tarnish film is Cu_2O with a tendency for (110) planes to lie parallel to the surface of the sample. (Courtesy H. R. Nelson, Battelle Memorial Institute.)



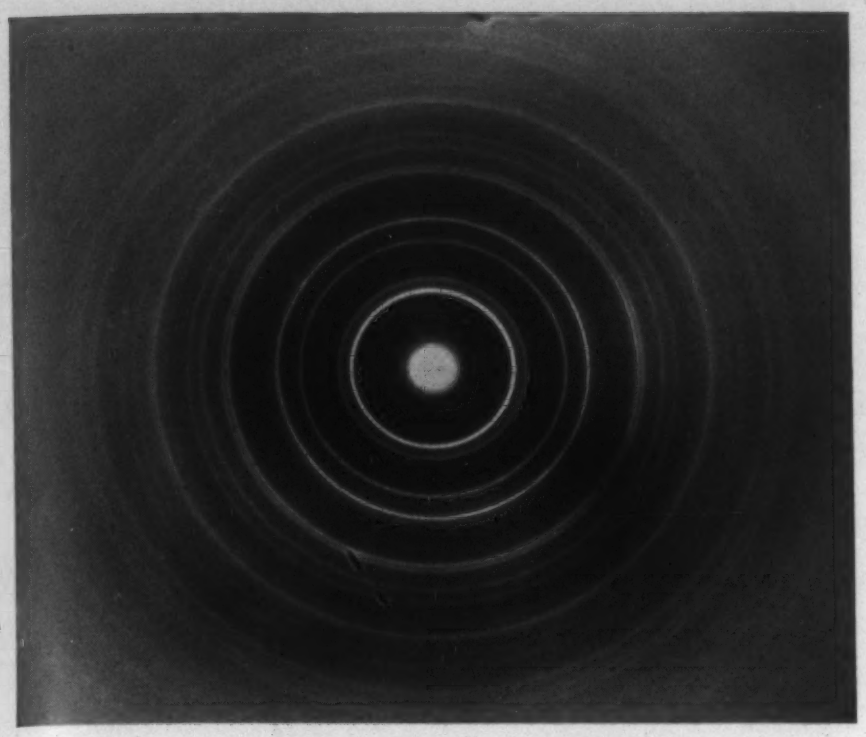


Fig. 12. Foil of Metallic Silver, Transmission Pattern. (Courtesy L. H. Germer, Bell Telephone Laboratories)

The large number of sharp rings in this typical transmission picture is an indication of the high resolution obtainable from properly prepared samples.

sively regular (atomically speaking), such as adsorbed gases, molecular layers of many organic materials, etc., can not be studied satisfactorily, for diffraction is essentially a "crystalline" phenomenon. Germer[41] has published a paper on the problem of adsorbed gas films on a single crystal. The apparatus used is quite different from that described heretofore, especially in that a Faraday box rather than a photographic plate is used to collect the diffracted electrons, and the interpretation is quite different; low speed electrons only have been employed. Such films present a very difficult and not too promising problem.

4. The use of a high vacuum makes any study of volatile layers futile. This may often be a severe handicap, for many cases of adsorption are likely to be so affected.

5. The difficulty of determining the composition of a film from its diffraction pattern is very serious. The crystal structure can be established from observed data, but these must be compared with the X-ray data of known compounds or, rarely, compared directly with a standard pattern. The experiments of Murison[42] illustrate the difficulties involved. He polished small blocks of copper on one face, heated them to various temperatures, and investigated the surface. He found patterns due to Cu_2O, CuO, and an unknown compound which formed after heating to 930 deg. F., and quenching in air. From X-ray data, he knew what to expect from Cu_2O, and from CuO, and he had no trouble in identifying them. The third compound, however, stopped him; he had used the only way known to him of making it, and there was no information available as to what it might be. However, much information concerning the films, even without absolute knowledge of the structure can be secured, for the physical nature of the surface is often more important than the chemical.

6. It is frequently difficult to interpret the patterns obtained; extra rings have occurred numerous times, and no one definite cause for them has yet been isolated. In some cases, the presence of both the film and metal pattern complicates matters, but on the other hand, it gives a clue to the thickness and coverage of the film. Nelson[12] found such interferences. On massive metals, very thin films may produce similar inconveniences[43] or may yield only the metal pattern. Also, an amorphous pattern is capable of many interpretations.

7. Certain structures are so similar in their diffraction effects as to be indistinguishable by such methods. Nelson cites the well-known example of Fe_3O_4 and γ-Fe_2O_3.

8. Other methods may be more suitable. It must be stressed that electron diffraction offers no panacea for corrosion ills; it is a powerful tool when properly used in conjunction with other tools. In addition to those mentioned before, X-rays, also, are very valuable, though the X-ray and electron diffraction procedures are usually not alternatives. Graf's work[44] on the corrosion at the surfaces of single mixed crystals illustrates the usefulness of this tool.

Conclusion

The foregoing paragraphs have attempted to interpret past achievements with a view toward predicting the future, and have outlined the obstacles in the way. It is difficult to say which of the applications here suggested will eventually become of commercial importance. Some undoubtedly will, while others may never advance beyond the present stage of development. Whatever the future of individual applications, however, a great general opportunity certainly exists. Electron diffraction has been largely employed by physicists and few attempts have been made to correlate the data. Nelson's paper[12] indicates that some engineers have already probed the subject in a systematic way. It is to be hoped that further engineering research into this fundamental question may, on the one hand, give us a keener insight into the mechanism of the corroding process, and on the other hand, may indicate the extent to which electron diffraction can be profitably employed.

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Letters to the Editor

"Non-Sparking" Beryllium Copper

To the Editor: In your February issue I have noted under the heading, "Current News Items," a brief comment concerning beryllium copper, which in the interest of accuracy I believe deserves clarification.

You have called attention to a recent announcement from the Riverside Metal Co., which states that, under certain conditions, the use of beryllium copper does not insure freedom from sparking. It is unfortunate that the wording of this announcement infers that beryllium copper itself can be made to throw friction sparks.

The term "non-sparking" as applied to beryllium copper was coined as a descriptive sales term some years ago by suppliers of bronze tools for use in the presence of highly inflammable vapors or liquids. It has long been recognized by safety engineers that the use of bronze tools in place of steel minimized the chances of obtaining friction sparks in such hazardous locations.

When beryllium copper was introduced early in 1932 it was soon recognized that the high physical properties of this heat treatable alloy would make a superior hand tool for work of this nature. Containing approximately 98 percent copper, it was readily appreciated that the alloy itself would not spark and could therefore be called "non-sparking". Many laboratory tests have confirmed this.

However, when applied to any non-ferrous tool, whether bronze or beryllium copper, the term "non-sparking" is probably a relative one. It is, of course, possible that even though a hammer itself does not spark there is a slight chance that a particle of ferrous metal being struck might fly off as a spark. The possibility of obtaining such a spark, and particularly of obtaining a spark of sufficient intensity to cause ignition of inflammable materials, is very much less when striking a non-ferrous material such as beryllium copper against steel than is the case when using steel against steel.

Since many chemical and oil companies are using beryllium copper tools because of this safety feature, it is important that these facts be clearly understood.

LOUIS L. STOTT,
Sales Manager

The Beryllium Corp. of Pa.,
Reading, Pa.

"Heredity" in Pig Iron

To the Editor: I would like to point out with reference to the title of an abstract—"Heredity of Blast Furnace Iron"—page MA 730 in the December issue, the flagrant misuse of the term "heredity." The reduction of silicon to close the grain and prevent porosity is so old and well known as a chemical change in the iron that this should not in any way be confused with heredity.

JAMES T. MACKENZIE,
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American Cast Iron Pipe Co.,
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Ductility of Creep-Resistant Steel at Elevated Temperatures

To the Editor: In a paper on "Creep and Engineering Design" presented before the International Association for Testing Materials in London, April, 1937, Bailey states:

> "Appreciable weakening of the steel may occur in time, and evidence shows that probably all low-alloy high creep-resistant steels fail under creep conditions by inter-crystalline cracking with comparatively low ductility." Further, " . . . total creep should not exceed 0.005 strain for high creep-resistant steels containing molybdenum."

These statements are based upon the results of creep-to-fracture tests carried out at the National Physical Laboratory under stresses from 20,000 to 34,000 lbs. per sq. in., a range of stress many times higher than that to which this type of steel is normally subjected, either in creep testing or service. Under these severe conditions, the specimens showed early intergranular failure with comparatively low ductility; the corresponding creep rates were abnormally high, ranging from 20 to 4000 millionths in./in./hr. (20 to 4000% per 10,000 hrs.). An identical test which we carried out gave results similar to those referred to by Bailey.

There is thus no question of the observations, but we are unable to agree with Bailey's interpretation of the data as applicable directly to service conditions where the working stress is much lower and the creep rate correspondingly smaller. Indeed, in our tests on this and similar steels in this temperature range, there has been in many cases a strain much greater than 0.005—that is, 0.5 per cent—yet with no indication of intergranular cracking or of failure. As a specific example, a low carbon, 0.5 per cent molybdenum steel in the spheroidized condition, subjected at 1100 deg. F. to a stress of 4000 lbs. per sq. in., elongated 4.2 per cent in 3500 hrs.; the stress was then raised to 7500 lbs. per sq. in. which caused failure 700 hrs. later with 103 per cent total elongation. This failure was transgranular, with no evidence whatever of intergranular oxidation or cracking. In similar tests on a variety of low-alloy steels, there was up to 6 per cent elongation over a period of about 3000 hrs., yet with no signs of intercrystalline cracking or fracture.

We submit therefore that rapid creep tests, such as those referred to by Bailey, cannot be directly interpreted in terms of what is to be expected under service conditions, for the reason that in these tests the stress is too high, and the time too short, to permit the metal to adjust itself by the relatively slow structural rearrangement which, under service conditions, permits flow without cracking.

R. H. ABORN and R. F. MILLER.
Metallurgists

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United States Steel Corp.,
Kearny, N. J.